

SPAWAR



*Systems Center
San Diego*

TECHNICAL REPORT 1768
April 1998

**Seawater Polynuclear
Aromatic Hydrocarbons and
Copper in San Diego Bay**

C. N. Katz

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Systems Center
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Space and Naval Warfare Systems Center
San Diego, CA 92152-5001

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ADMINISTRATIVE INFORMATION

The work detailed in this report was performed for the Navy Energy and Environmental Support Activity by the Marine Environmental Quality Branch, Code D362, Space and Naval Warfare (SPAWAR) Systems Center, San Diego (SSC San Diego).

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EXECUTIVE SUMMARY

Water quality measurements were made throughout San Diego Bay in 1997 as part of the Navy's efforts to assess current environmental conditions in the bay. The water quality measurements focused on polynuclear aromatic hydrocarbons (PAH) and copper (Cu) concentrations, compounds that have been identified as chemical contaminants of concern by the San Diego Bay Interagency Water Quality Control Panel. The effort was designed to assess how recent changes in bilge water operations and the removal of creosote impregnated pier pilings at Naval Station, San Diego (NAVSTA), may have impacted the steady-state concentrations of these contaminants in the waters of San Diego Bay.

Measurements were made during two dry-weather surveys using the unique capabilities of the Navy's Marine Environmental Survey Capability. Discrete samples collected for PAH and Cu were augmented with real-time, high spatial resolution measurements provided by MESC. In this way, MESC provided integrated, full bay coverage of contaminant levels as well as the hydrographic and general water quality conditions needed to characterize sources. For the most part, bay hydrographic conditions were consistent with historical measurements. The main exception was elevated suspended loads at the entrance to the bay and within Commercial Basin where dredging operations were underway. From a standpoint of assessing the impact of source reductions at NAVSTA, the bay was considered to be in steady state.

Total PAH concentrations ranged from 35 to 200 ng·L⁻¹ and 24 to 130 ng·L⁻¹ on the two surveys. Concentrations increased moving into the bay, typically to maximum levels in the vicinity of NAVSTA. Based on PAH analyte fingerprinting, the seawater samples were characterized as predominantly weathered creosote. An exception to this occurred at one NAVSTA site at which the source appeared to be chronically derived from both weathered creosote and fuel product sources in roughly equal amounts. Dissolved Cu concentrations, measured only on one survey, ranged from 0.41 to 4.18 ug·L⁻¹. Concentrations that generally increased into the back bay were augmented with local increases in the vicinity of semi-enclosed basins and at NAVSTA.

From a regulatory perspective, nearly all the measured PAH were below Environmental Protection Agency (EPA) water-quality criteria proposed for California. Only two stations at NAVSTA on the first survey had any analyte above the criteria. No PAH analytes surpassed criteria on the second survey. Nearly half the bay had Cu concentrations that surpassed the proposed limit of 3.1 ug·L⁻¹.

Concentrations of PAH were the lowest measured in the bay in the last 8 years. Recent PAH levels at NAVSTA sites compared with those measured historically are significantly lower by a factor of nine. Non-NAVSTA sites were also significantly lower by more than a factor of two. Based on the historical distribution of sources and source types, the reduction in PAH concentrations at NAVSTA sites and, perhaps, the rest of the bay, can be attributed directly to the change in operations at NAVSTA. While recent Cu concentrations were not statistically different from those measured historically at NAVSTA sites, the remainder of the bay had significantly lower concentrations. Operational changes at NAVSTA have not impacted Cu concentrations in the bay.

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ACRONYMS

Chl-a	Chlorophyll-a
COMNAVBASE	Commander, Naval Base San Diego
Cu	Copper
DFME	Diesel fuel marine equivalents
EPA	Environmental Protection Agency
MESC	Marine Environmental Survey Capability
NAVSTA	Naval Station, San Diego
PAH	Polynuclear aromatic hydrocarbons
PSA	Potentiometric stripping analysis
rsd	Relative standard deviation
SDGE	San Diego Gas and Electric
TMA	Trace metals analyzer
TPAH	Total polynuclear aromatic hydrocarbons
TSS	Total suspended solids
uv	ultra-violet

INTRODUCTION

With its large presence on the City of San Diego's waterfront, particularly at Naval Station, San Diego (NAVSTA), the U.S. Navy is a major stakeholder in the environmental protection of San Diego Bay. Because of environmental concerns, NAVSTA recently altered operations so that bilge water previously discharged into gravity separators open to the bay is now collected and treated ashore. Additionally, there is now a concerted effort to replace creosote-impregnated and copper-treated pier pilings with plastic, concrete, or untreated pilings, depending on structural and engineering requirements. So far, roughly half of the pilings have been replaced. Because these practices may improve receiving water concentrations of polynuclear aromatic hydrocarbons (PAH) and Copper (Cu), Commander Naval Base (COMNAVBASE) San Diego, requested a study to quantify how these operational changes affected PAH and Cu levels in the bay.

BACKGROUND

PAHs make up a class of organic compounds containing two or more fused rings commonly found in fuels and combustion products while Cu is an inorganic heavy metal found in the earth's crust. Both materials were identified as chemical contaminants of concern by the San Diego Bay Interagency Water Quality Panel, the technical advisory panel to the Regional Water Quality Control Board. Sources of PAH to the bay included oil spills, bilge water discharge, atmospheric deposition, storm water runoff, sediment flux, leaching from creosote-impregnated pier pilings, and compensating fuel system discharges. Sources of copper to the bay included storm water runoff, sediment flux, atmospheric deposition, leaching of, and in-water hull cleaning of copper-based, anti-fouling paints, and cooling water discharge from the San Diego Gas and Electric (SDGE) power plant. While the sources of these compounds were identified, their loading terms were not well quantified (PRC, 1997; Woodward-Clyde, 1996; Chadwick et al., 1996). Without good loading information, monitoring their concentrations in the bay may provide useful information in determining the bay's assimilative capacity for these contaminants.

Historically, the primary source of PAH to San Diego Bay has been leaching from creosote-impregnated pier pilings (Katz et al., 1995; Woodward-Clyde, 1996; Chadwick et al., 1996). The seawater distribution of PAH consistently showed higher concentrations of PAH in the back bay (the region south of the Coronado Bay Bridge), particularly in the vicinity of NAVSTA, where pilings are most plentiful, seawater temperatures are highest (higher leach rates), and flushing is relatively low (Katz et al., 1995;). The back bay is also where the majority of storm water runoff enters and where NAVSTA bilge water operations have historically introduced PAH to the bay. These sources have led to historic seawater PAH distribution chronically elevated in the vicinity of NAVSTA. Fingerprinting the seawater PAH data confirmed that the sources were typically derived from a combination of weathered creosote and diesel products (Katz et al., 1995).

The primary source of Cu to the Bay has been its release from copper-based, anti-fouling paints used on ship hulls. It is estimated that passive leaching and its release during in-water hull cleaning provide almost 80% of the copper loading to the bay (Valkirs et al., 1994; PRC, 1997). Moving in from the entrance to the bay, the principal locations of vessels include: Sub Base San Diego; Shelter Island Basin; Commercial Basin; Harbor Island East and West Basins; the Aircraft Carrier Piers on Coronado Island; Marriott Marina; Glorietta Bay; NAVSTA; Coronado Cays; and the Chula Vista Marina (figure 1). Of the Cu released from hull paints, 80% is estimated to come from pleasure craft,

with the remainder from U.S. Navy vessels (PRC, 1997). The semi-enclosed yacht basins in the bay should, thus, be the locations of highest seawater Cu concentrations.

Given the historical sources and distributions of PAH and Cu in San Diego Bay, COMNAVBASE recognized that a unique opportunity existed to quantify how changes in NAVSTA operations might affect receiving water conditions. COMNAVBASE tasked the Marine Environmental Sciences Division of the Space and Naval Warfare Systems Center, San Diego to perform this assessment.

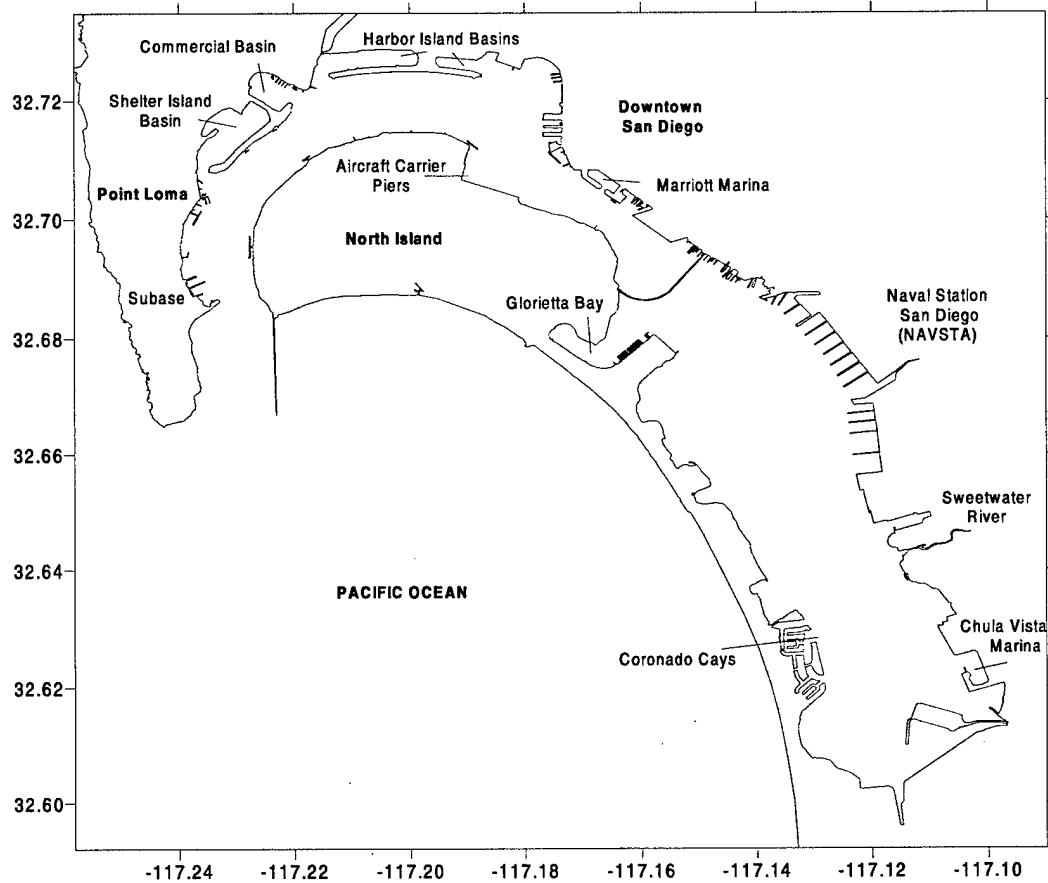


Figure 1. San Diego Bay study area.

TECHNICAL APPROACH

The technical approach taken was to make measurements of seawater PAH and Cu concentrations in the bay to monitor current water quality conditions and to compare them with historical measurements. Measurements were made during two dry-weather surveys using the unique capabilities of the Navy's Marine Environmental Survey Capability (MESC). The surveys were performed under dry weather conditions to ensure that concentrations in the bay were as close to steady state as possible. The MESC acquired near-synoptic, real-time, water quality data in addition to the collection of discrete seawater samples for chemical analyses. In particular, the MESC provided high-spatial resolution ultra-violet (uv) fluorescence data, a surrogate measure of PAH, and a trace metals analyzer (TMA) employing potentiometric stripping analysis (PSA) for Cu analysis. The two measurement techniques, when calibrated against the discrete sample analyses, provide a high-spatial-resolution data set that is important in mapping distributions.

Comparison of the new data with those collected historically was approached from a statistical viewpoint. Hypotheses were developed to test for changes in both bay-wide levels and for those data collected in the vicinity of NAVSTA. In statistical terms, the null hypothesis is that the present concentration levels of PAH or Cu in the bay are the same as those measured historically. The alternative hypothesis is that the present concentration levels are lower than those measured historically. If the null hypothesis is rejected, the present-day levels are statistically lower than those previously measured. However, the cause of the lower concentrations is derived only after review of current and historical seawater distributions, their spatial relation to sources, and assessment of source types.

METHODS

Water quality data were collected during two MESC surveys performed on 16 July and 4 November 1997. The MESC, installed aboard the RV *Ecos*, collected discrete seawater samples over a wide, though sparse, spatial range. These samples were analyzed with chemical analyses approved by the Environmental Protection Agency (EPA). The MESC also collected water quality data at a much higher spatial resolution using real-time sensors that were intercalibrated with the discrete seawater sample data. In the case of PAH, uv fluorescence of seawater was used as a surrogate for total PAH (TPAH), while PSA measured Cu. Combining methods allowed extension of the more costly discrete measurement data to a higher spatial resolution.

MESC data were collected along the tracks shown in figures 2 and 3 while moving at a nominal speed of 6 knots. The figures show discrete sample locations as closed circles. The two tracks differed in their southernmost extent, a result of a higher tidal condition on the first survey allowing the *Ecos* to go into the shallow waters in the southernmost part of the back bay. The number of discrete sites on the second survey increased from the 14 collected on the first survey to a total of 20, a result of adding discrete sample sites specifically for Cu analysis.

MESC REAL-TIME DATA

The MESC is a real-time data acquisition system designed and built by the Navy to provide integrated, rapid, continuous measurement and mapping of oceanographic and environmental parameters in coastal and estuarine environments (Lieberman et al., 1989; Chadwick and Salazar, 1991; Katz and Chadwick, 1993). The purpose of the MESC is to determine spatial and temporal variability of physical and chemical water quality characteristics from a moving vessel using state-of-the-art sensors, computer systems, and navigation equipment. This approach allows for direct, *in situ* measurements that avoid extrapolation and provides sequential measurements at a frequency commensurate with scales of natural and anthropogenic variability. The MESC, therefore, provides the near-synoptic real-time data collection necessary to effectively map the coastal environment's highly dynamic nature.

The MESC employs both a towed sensor package and a seawater flow-through system that provides a continuous seawater stream to a suite of onboard sensors. Sensors in the towed package consist of a conductivity, temperature, and depth profiler outfitted with pH and dissolved oxygen sensors, a light transmissometer, and an uv-fluorometer (254 nm excitation 300- to 400-nm emission) for oil (PAH) detection. A V-Fin depressor keeps the instrument package stable and submerged to the appropriate

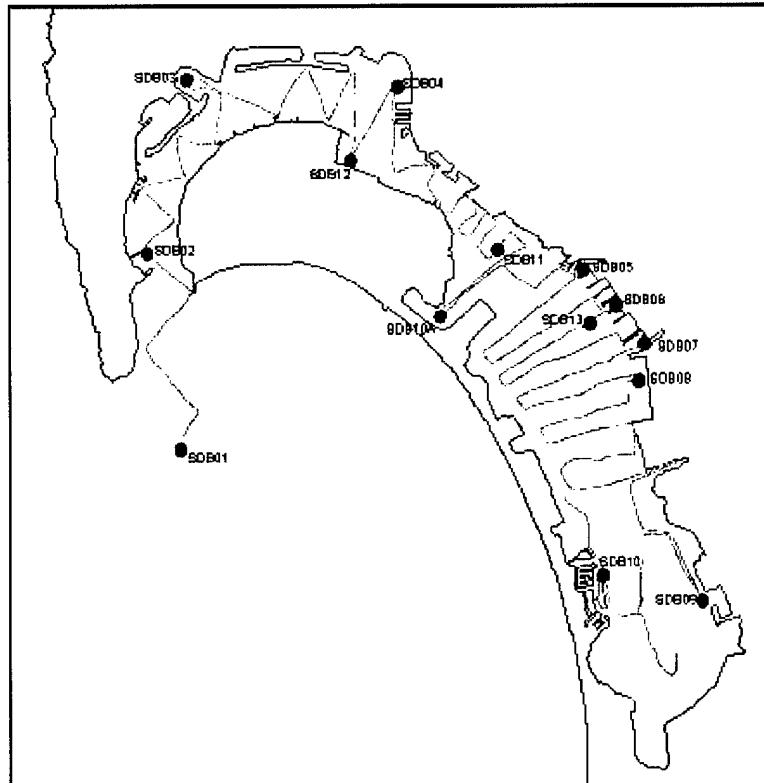


Figure 2. MESC survey trackline and discrete sampling sites for 16 July 1997.

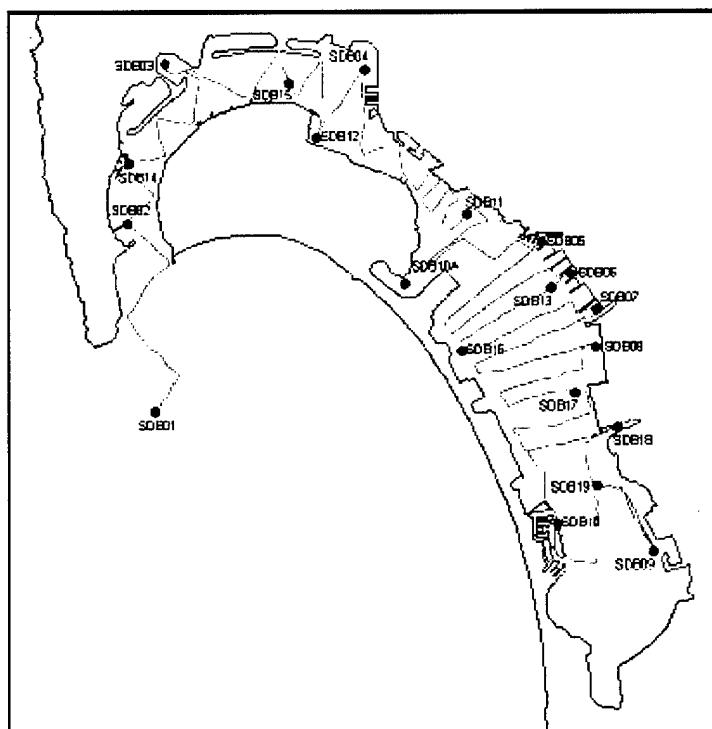


Figure 3. MESC survey trackline and discrete sampling sites for 4 November 1997.

depth, while a hydraulic winch raises and lowers the package to the desired water depth. The onboard sensors include multiple fluorometers, an automated TMA, an acoustic Doppler current profiler, a digital fathometer, and a differential Global Positioning System navigation receiver. The onboard fluorometers are independently set up to measure oil constituents (PAH) and chlorophyll *a* (chl-*a*).

MESC data acquired during the surveys included: location, salinity, temperature, sample depth, bottom depth, pH, dissolved oxygen, light transmission, Cu, uv-oil fluorescence, chlorophyll *a* fluorescence, current velocity, and wind velocity. These measurement data were used to calculate seawater density, oxygen saturation, and total suspended solids. Most data were collected at a 4-Hz sampling rate providing an along-tack spatial resolution of less than 1 meter. Those data collected at a 1-Hz rate (location, bottom depth, and wind velocity) were interpolated to the 4-Hz data rate. Current velocity data were averaged over a 10-s interval while the trace metals data were collected at a 6-min interval.

DISCRETE SEAWATER SAMPLE COLLECTION

Discrete seawater samples were collected at 14 sites on the first survey in July, while 20 sites were visited on the second survey in November (figures 2 and 3). *Ecos* stopped at each sampling site to ensure that the sample was collected at a single location. Seawater samples were collected for PAH, Cu, chl-*a*, and total suspended solids (TSS). The chl-*a* and TSS data were used to calibrate the real-time chl-*a* fluorometer and light transmissometer, respectively. All the real-time measurements were made continuously during the discrete sampling period to ensure that all the data could be co-located and integrated.

The MESC's all-TEFLON seawater flow-through system was used to obtain all discrete seawater samples. Seawater was pumped to the deck into pre-cleaned 2-L glass bottles for PAH, 250-mL polyethylene bottles for Cu, and 1-L polycarbonate bottles for chl-*a* and TSS. The PAH bottles were filled to preclude any headspace. Two sets of Cu samples were collected, one for outside contract lab analysis and one for discrete measurements on the TMA. All samples were stored in the dark at <10°C until analysis. The PAH and Cu samples were shipped on ice to contract laboratories the day after collection by overnight mail. A total of 28 PAH samples were obtained for analysis, 14 on each survey. A total of 20 Cu samples were obtained on the November survey. One PAH sample was broken during shipment, so 27 PAH samples and 20 Cu samples were analyzed. The 14 samples collected in July for TSS and Chl-*a* were analyzed and used for calibration purposes for both surveys because the samples collected in November were lost when they were inadvertently thawed. Because historical calibrations for the light transmissometer and chlorophyll *a* fluorometer are used in the calibration process, and because relative values are the critical component, samples collected on the first survey were sufficient for calibration purposes.

DISCRETE SAMPLE CHEMICAL ANALYSES

Polynuclear Aromatic Hydrocarbons

PAH samples were analyzed using the National Oceanic and Atmospheric Administration's Status and Trends version of the EPA Method 8270M, SIM by A. D. Little in Cambridge, MA. Upon arrival, samples were acidified to pH 2.0 with 6N HCl, spiked with PAH surrogates, then solvent-extracted in dichloromethane using a method similar to EPA Method 3501B, Separatory Funnel Liquid-Liquid Extraction. The extracts were dried using sodium sulfate and concentrated to approximately 1 mL using Kuderna-Danish concentrators followed by nitrogen evaporation.

The concentrated samples were analyzed by Gas-Chromatography-Mass-Spectrometry run in Single Ion Mode. A total of 41 individual PAH analytes were each quantified at $10 \text{ ng}\cdot\text{L}^{-1}$, except for naphthalene and phenanthrene, which had blank spikes of $17 \text{ ng}\cdot\text{L}^{-1}$. Quality Assurance/Quality Control analyses showed matrix spike recoveries between 60 and 117%, with an average of 82%. Checks made against standard reference oils showed analytes within 25% (average of 3.4%) of targeted values. The methods used and the full results of these analyses are included in appendix A.

Copper

Battelle Marine Sciences Laboratory in Sequim, WA analyzed dissolved Cu samples using EPA Method 1640. Upon arrival at Battelle's laboratory, the samples were filtered through a $0.45\text{-}\mu\text{m}$ capsule filter and acidified with 10% HNO₃ to bring the sample to a pH <2. The filtered samples were then preconcentrated by tetrahydroborate reductive precipitation (Nakashima et al., 1988) and determined by Inductively Coupled Plasma-Mass Spectrometry.

The method detection limit for these analyses was $0.1 \text{ ug}\cdot\text{L}^{-1}$. Quality Assurance/Quality Control analyses resulted in replicate analyses of less than $\pm 3\%$, blanks less than $0.06 \text{ ug}\cdot\text{L}^{-1}$, matrix spike recoveries of >99%, and an analysis of a Standard Seawater Reference Material within 29%. Two samples that were spilled during filtration and gave unusually high values were considered compromised and not used further. The methods used and the full results of these analyses are included in appendix B.

Seawater samples were analyzed for copper using the TMA in both a discrete mode and in a continuous real-time mode. In discrete mode, seawater was drawn into the analyzer from a sample bottle while in continuous mode, the sample was drawn directly from the MESC seawater flow-through about every 6 minutes. The discrete samples, taken at the same time as those to be analyzed by EPA methods, were analyzed at the end of the day. In both modes, the analyzer automatically analyzed the seawater for copper using potentiometric stripping analysis methods. A 3-mL aliquot of water was brought into an electrochemical cell along with chemical reagents to facilitate the analysis. A negative potential was applied to the solution using a mercury film electrode that binds the copper in solution. The electrode potential was then reversed and the copper was driven off at its characteristic voltage. The concentration of copper was determined by the length of time it remained bound to the film at its characteristic stripping potential.

TSS and Chl-a

Samples collected for TSS were analyzed by filtering approximately 900 mL through pre-dried and pre-weighed glass-fiber filters (1.2-um nominal pore size). The filters were rinsed with deionized water to remove dissolved salts, then dried and weighed to determine the mass of the filtered solids. Samples collected for chl-a were analyzed using standard techniques described in ASTM (1995). Seawater was filtered through microfiber filters and the filtrate extracted in 90% acetone. The solution was analyzed on a Turner designs Model 10 fluorometer that was calibrated using a standard chl-a reference standard. The sample was analyzed before and after acidification with HCl to account for pheophytin interference.

DATA INTERCALIBRATIONS

Real-time sensor data were intercalibrated with discrete sample measurement data to derive absolute calibration and/or to provide correlation data that could enhance the spatial resolution of the more limited, more costly, and time-consuming traditional analyses. In the case of chl-a, discrete

samples analyzed with traditional laboratory methods provide an absolute calibration for the real-time flow-through fluorometers. Similarly, the discrete analyses for dissolved Cu provided an absolute calibration for the real-time TMA Cu data. Discrete samples analyzed for PAH data were used to develop a regression equation with uv-fluorescence data, a relationship that previously was found to be well correlated with TPAH ($r^2=0.81$) by Katz et al. (1991). Similarly, discrete samples analyzed for TSS data were used to develop a regression equation between TSS and light transmission data. A database developed over the past 5 years showed these two variables to be well correlated ($r^2=0.90$).

The intercalibrations were typically performed by comparing the average value of the real-time sensor data collected during each sampling interval with the discrete sample value. The hose lag was taken into consideration when computing the average value. In the case of Cu, the splits taken during sampling were analyzed on the TMA in discrete mode and compared to the analyses performed by the contract laboratory. The regression equations developed for each set of measurements are described in the Results section.

RESULTS

GENERAL WATER QUALITY PARAMETERS

The two MESC surveys were performed under weather conditions typical of the summer and fall seasons. Both survey days started out with calm winds and overcast skies that gave way to light breezes and sunny skies later in the day. Air temperatures were seasonably warm with winds generally out of the south-southwest, averaging less than 10 knots. Sea conditions were calm both early and late on each survey day, with about a 0.3-m wind chop during the mid-day period.

The surveys were performed during dry weather periods to minimize the impact of runoff sources. The last measurable rainfall prior to the July survey was in April when 0.28 inch of rain was reported at Lindbergh Field (Monthly Climate Summaries for San Diego). For the November period, the last measurable rainfall of 0.02 inch fell in October, though 0.85 inch fell in September. Measurements were also made during low to medium tidal amplitudes (<1.1 m) to minimize the effects of current velocities on the distributions. Measured currents averaged about $11 \pm 9 \text{ cm} \cdot \text{s}^{-1}$ throughout the bay on both surveys. With respect to storm water input and tidally driven transport, the bay could be reasonably assumed to be at steady state during the measurement period.

Seawater conditions in San Diego Bay measured in 1997 were consistent with those observed in the past (Lapota et al., 1993; Chadwick et al., 1996). Figures 4 and 5 show that both temperature and salinity values increased from the entrance into the back bay. The gradient was strongest in July when solar insolation heats the shallow back bay waters and evaporation far exceeds the negligible summer precipitation or fresh-water input. The additional heat generated by the SDGE power plant enhances this gradient. The data collected at the outflow of the SDGE plant were collected only in July when tide conditions were appropriate to move *Ecos* into very shallow water. The data showed a decrease in both absolute values as well as the gradient in both parameters from July to November, as expected with seasonal climate changes.

Chl- α concentrations, derived from the regression equation,

$$\text{Chl-}\alpha \text{ (}\mu\text{g L}^{-1}\text{)} = 0.0090 \cdot \text{Fluorometer volts} + 0.0048 \text{ (\textit{r} }^2 = 0.72\text{),}$$

were relatively high in July, ranging from about 4 to 12 $\mu\text{g}\cdot\text{L}^{-1}$. Maxima were seen in Commercial Basin and in the back bay (figure 6). These data were considerably higher than those measured during a similar summer period in 1993 but were not out of the range seen at other times of the year (Lapota et al., 1993). While chl- α data were available for only the back bay region in November, the distribution still showed a general increase in concentration levels going into the back bay, particularly on the shallower western side. On this survey, a maximum in the chl- α distribution was observed at the entrance to the Sweetwater Channel.

Dissolved oxygen concentrations ranged between 3.9 and 5.5 $\text{mL}\cdot\text{L}^{-1}$ and were typically between 83 and 110% of atmospheric equilibrium saturation values. Consistent with the effects of temperature and salinity on equilibrium, oxygen values generally decrease into the back bay, though not uniformly (figure 7). An oxygen high was observed in the November data set at the entrance to Sweetwater Channel. This increase, coincident with pH and chl- α maxima, suggests that a bloom condition was occurring.

TSS concentrations for these surveys were derived from a regression of light transmissometer data with discrete samples measured for TSS. The data collected on the July survey were added to a calibration database for the transmissometer that goes back to 1993. A log-linear regression using the complete instrument calibration of 173 data points gave the regression equation of:

$$\text{TSS (mg}\cdot\text{L}^{-1}\text{)} = 90.498 \cdot e^{-0.1271 \cdot \text{Transmission (\%)}} \quad (r^2=0.90).$$

The distribution of TSS observed in July shows a general increase in concentrations moving into the bay from the entrance, from about 1 to 6 $\text{mg}\cdot\text{L}^{-1}$ (figure 8). This typical distribution was altered considerably in November by dredging operations that were in progress at the entrance to the bay, and within Commercial Basin. Concentrations in November were as high as 14.5 $\text{mg}\cdot\text{L}^{-1}$ along the eastern shore of Point Loma. These unusually high suspended loads fell off in the mid-bay region.

With the exception of the high suspended loads seen at the entrance to the bay in November, the water quality conditions observed during the two surveys are consistent with historical measurements. An August 1992 MESC survey collected under comparable climatological and hydrographic conditions showed distributions (figure 9) and average values similar to those seen in the two 1997 surveys. Having both the current and historical water quality measurements made throughout the bay provides the necessary data to evaluate the reasonableness of steady state. With the exception of the entrance area in November that was impacted with high suspended loads from dredging operations, the bay, in general, and the NAVSTA area, in particular, appeared to be reasonably at steady-state during both 1997 surveys.

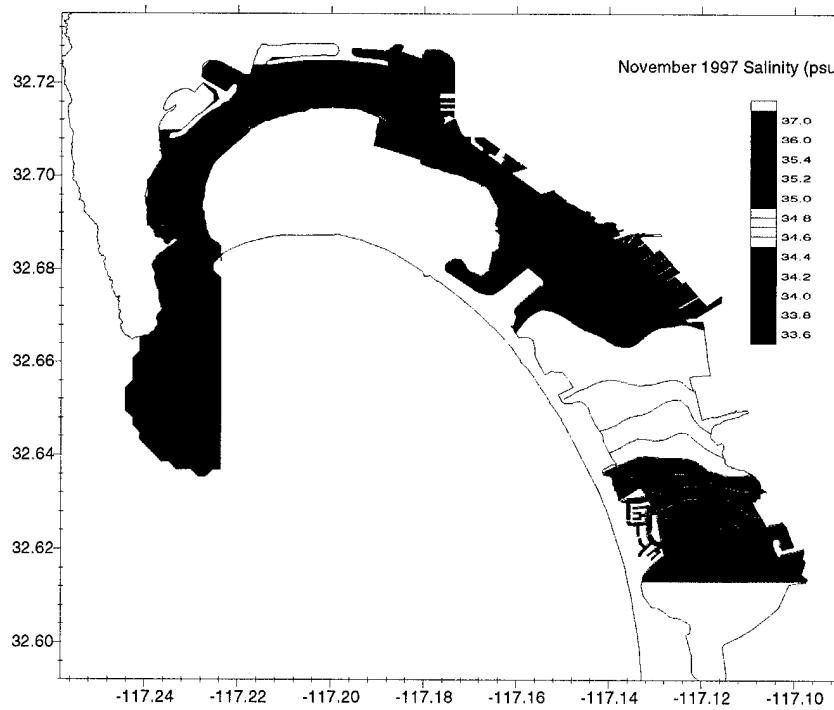
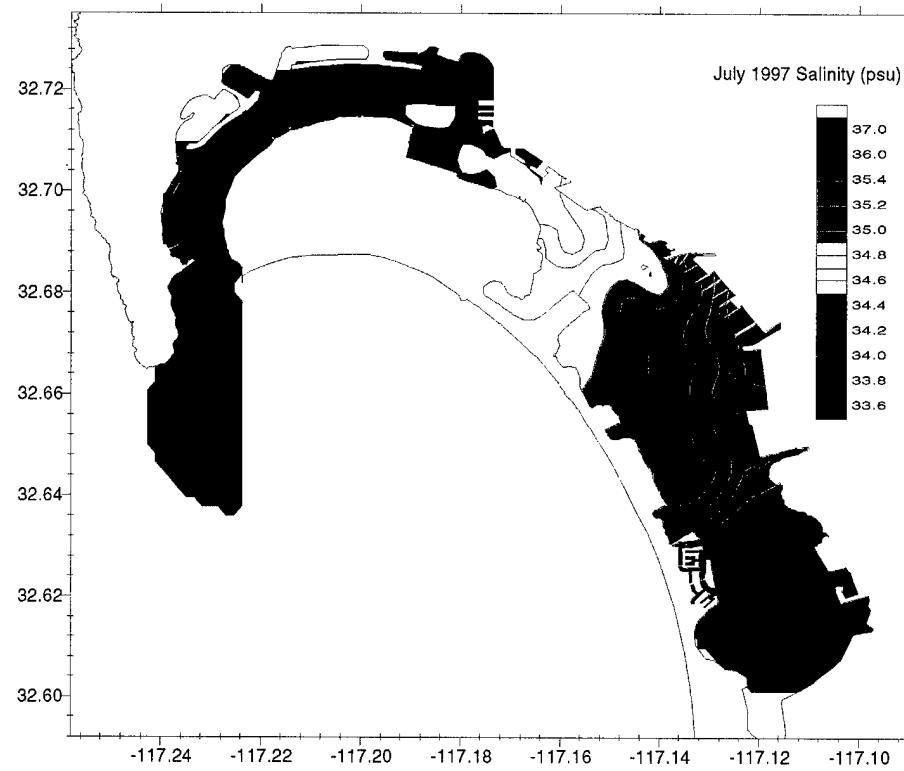


Figure 4. Salinity (psu) distribution for 16 July and 4 November 1997 MESC surveys.

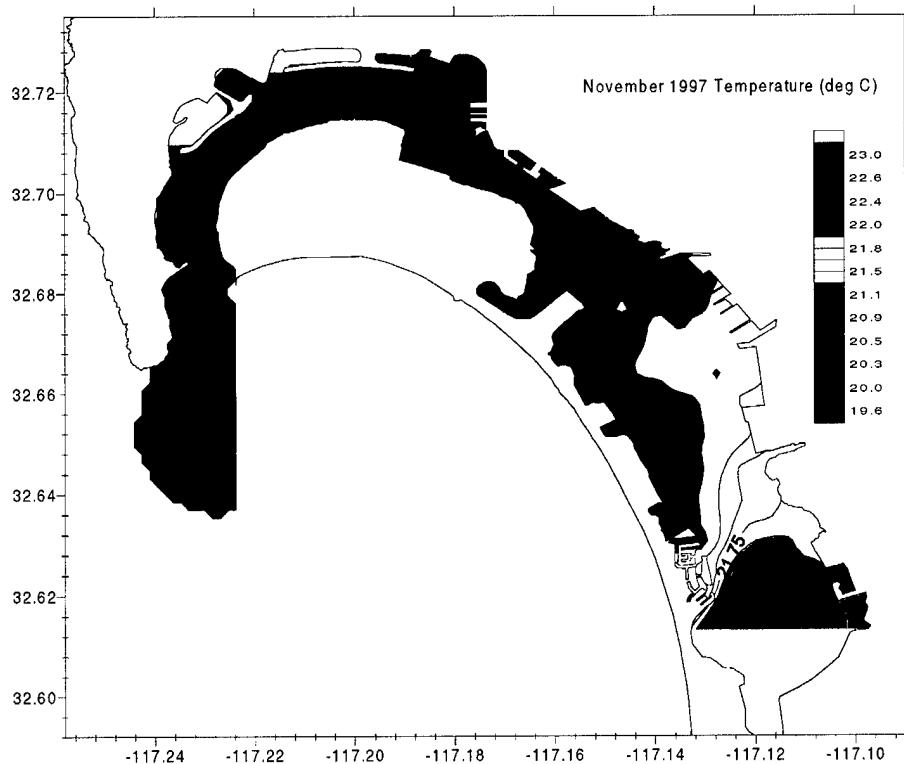
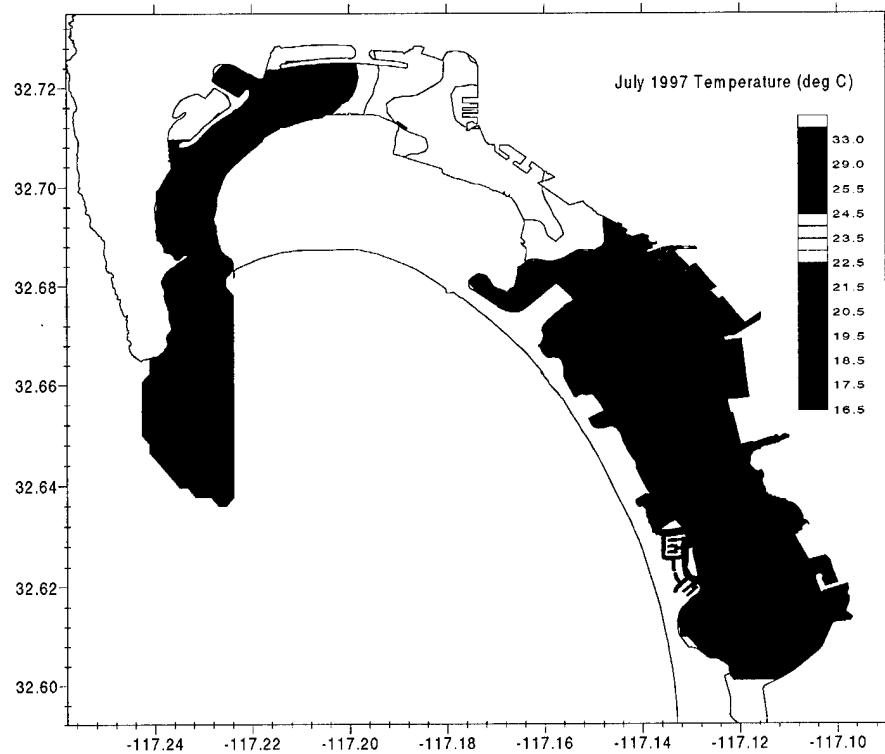


Figure 5. Temperature (degrees Centigrade) distribution for 16 July and 04 November 1997 MESC surveys.

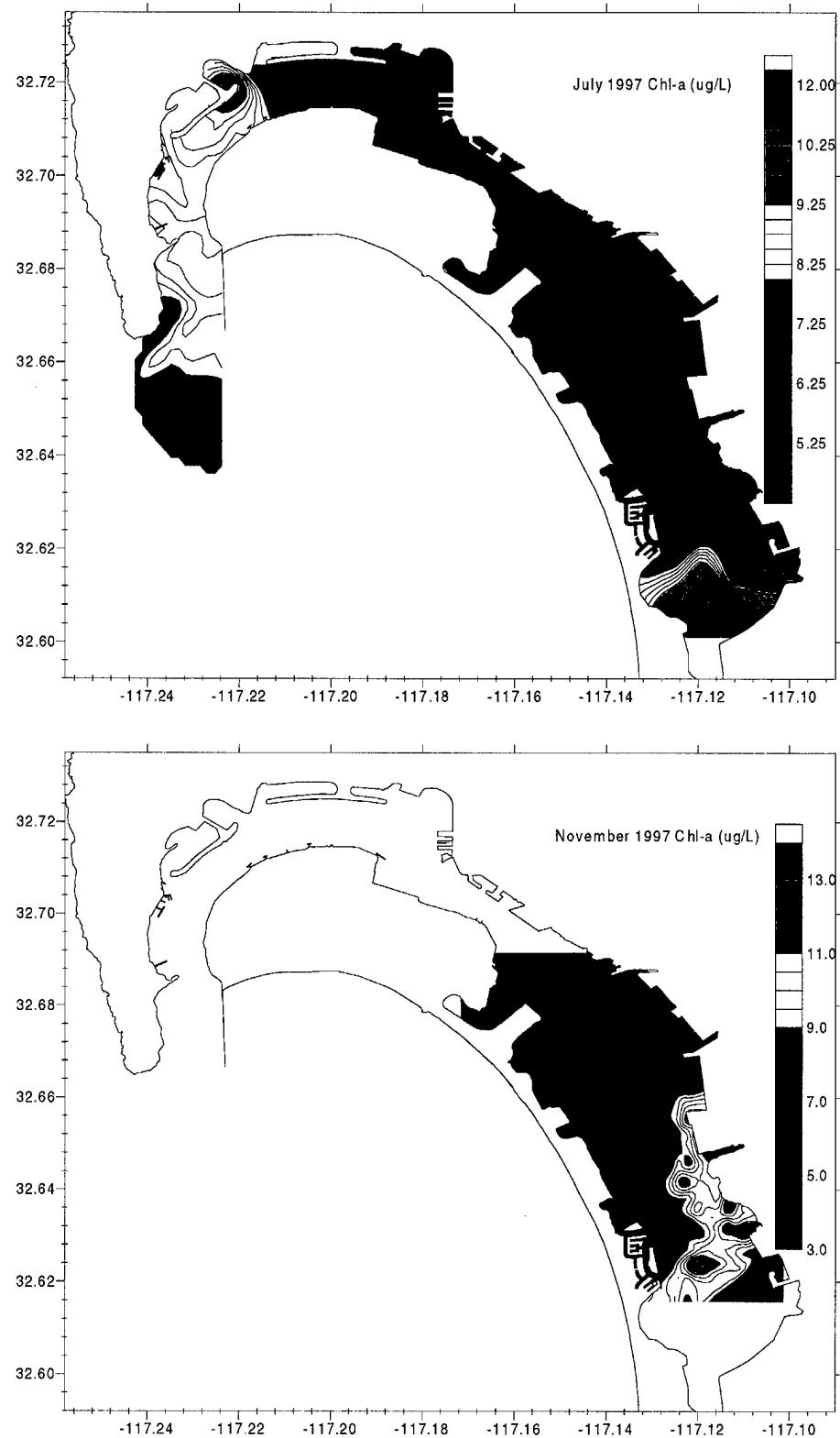


Figure 6. Chlorophyll-a distribution for 16 July and 4 November 1997 MESC surveys. Data were collected in the front bay.

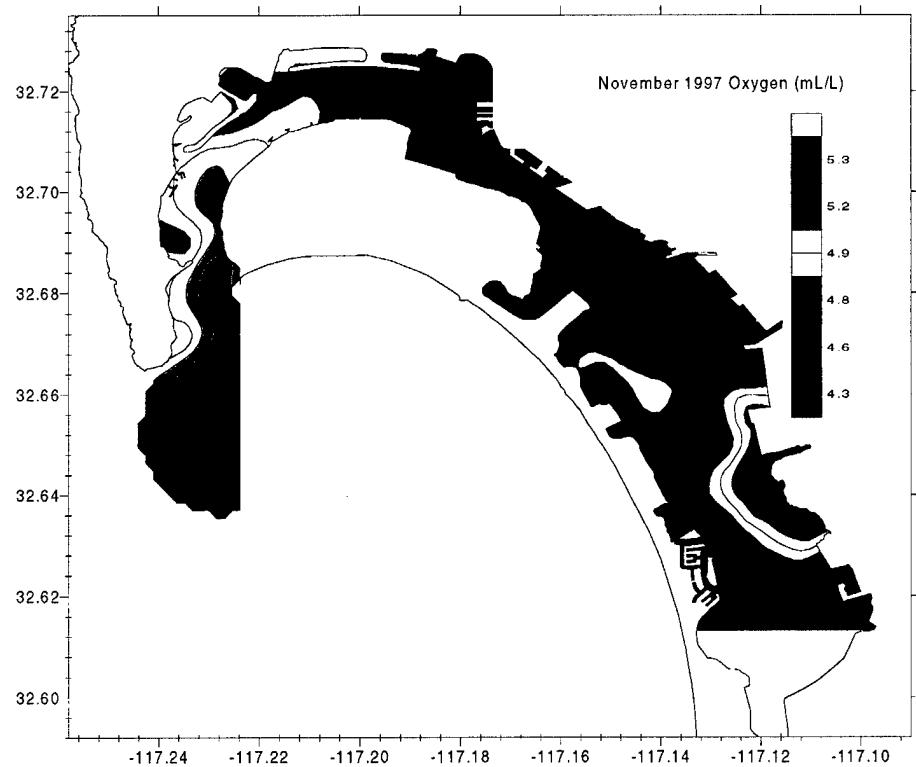
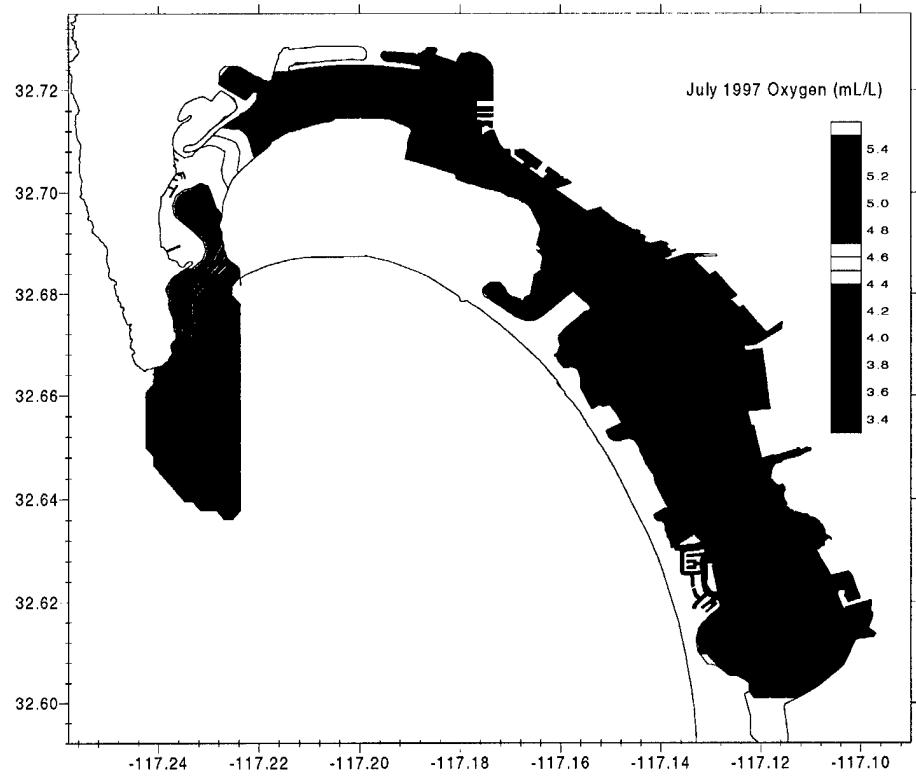


Figure 7. Dissolved oxygen ($\text{mL}\cdot\text{L}^{-1}$) distribution for 16 July and 4 November 1997 MESC surveys.

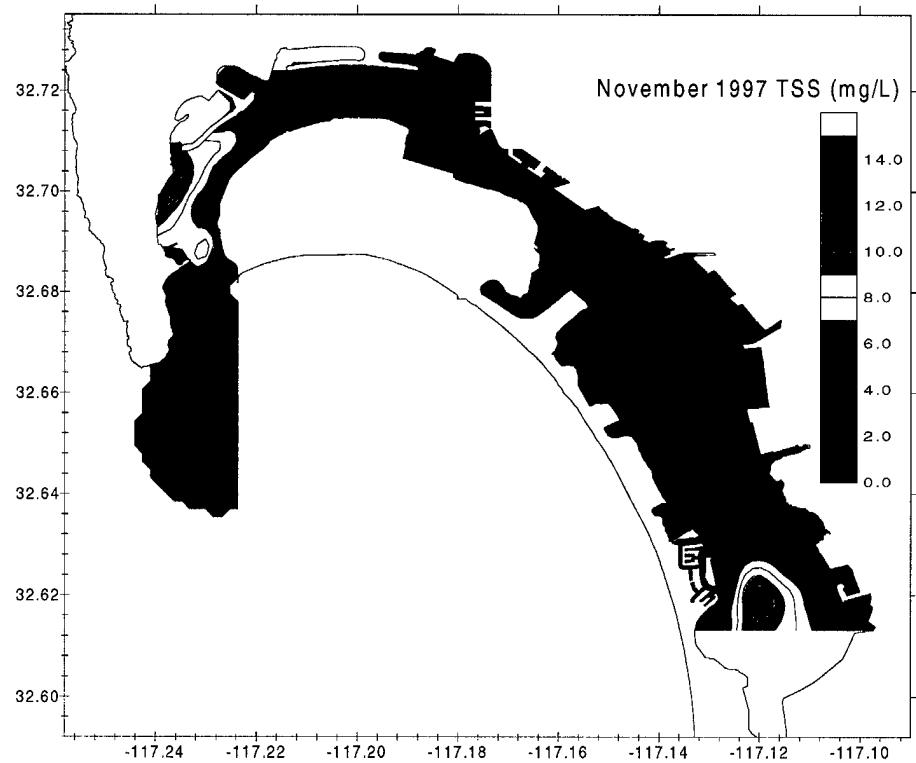
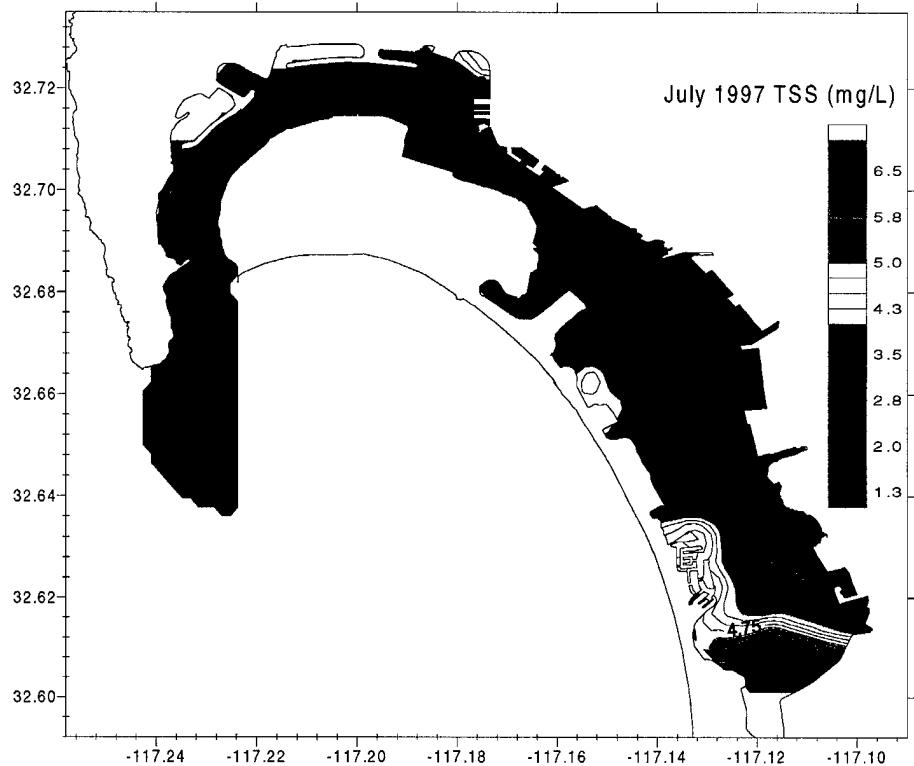


Figure 8. Total suspended solids (mg/L) distribution for 16 July and 4 November 1997 MESC surveys.

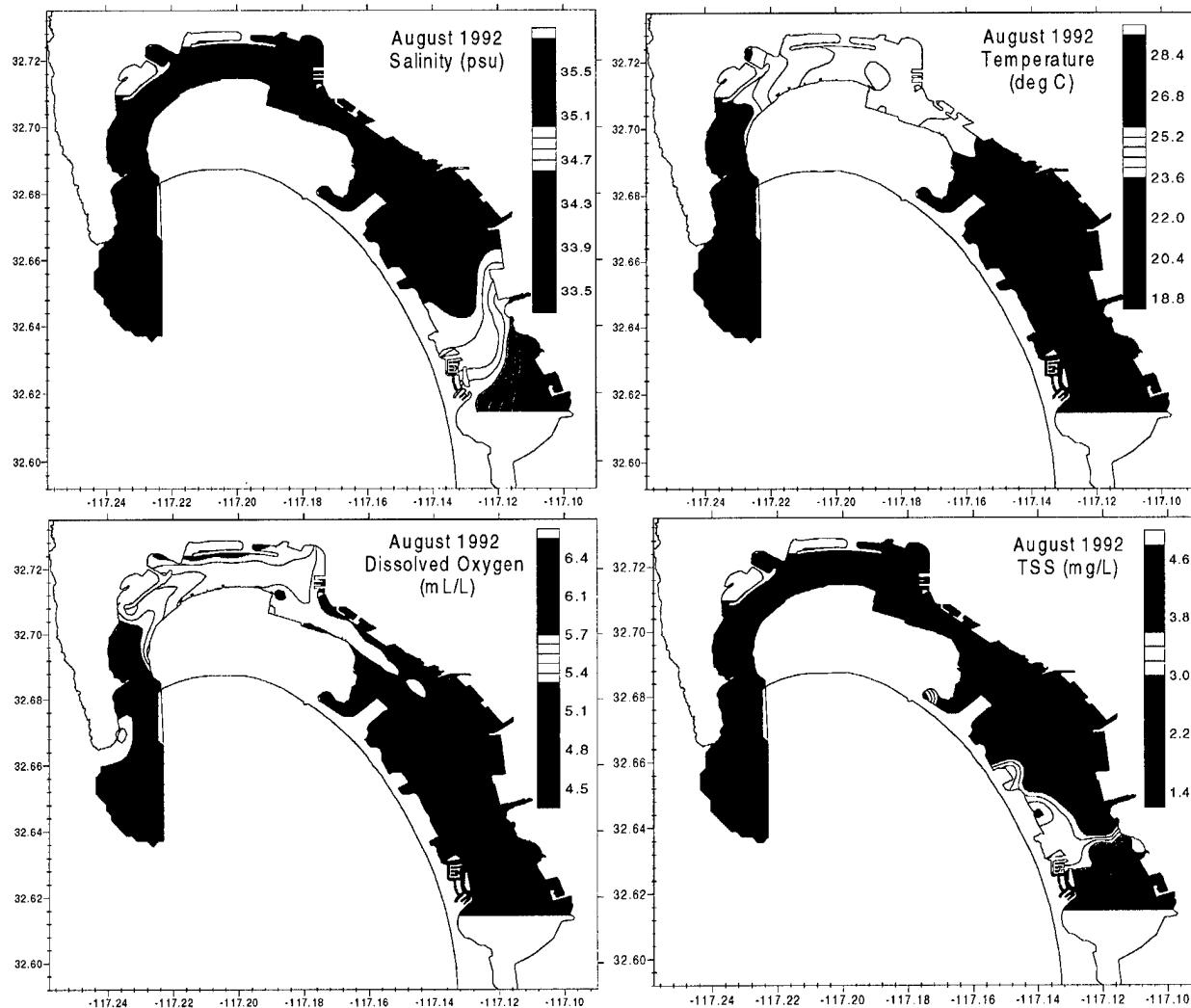


Figure 9. Distribution of salinity (psu), temperature (degrees Centigrade), dissolved oxygen ($\text{mL}\cdot\text{L}^{-1}$), and TSS ($\text{mg}\cdot\text{L}^{-1}$) for 20 August 1992.

POLYNUCLEAR AROMATIC HYDROCARBONS

Table 1 and figure 10 show the seawater PAH data collected on the two 1997 surveys in terms of TPAH concentrations. Concentrations ranged from $35 \text{ ng}\cdot\text{L}^{-1}$ in July and from $24 \text{ to } 130 \text{ ng}\cdot\text{L}^{-1}$ in November. On average, concentrations were lower on the second survey by 25% though two sites (SDB03 and SDB12) were actually higher on the second sampling. Maximum concentrations were observed at the four NAVSTA sites (SDB05 to SDB08) in July. While the NAVSTA sites remained elevated in November, a maximum TPAH concentration was observed in Commercial Basin (SDB03). The high PAH seen at this site was coincident with ongoing dredge operations.

Table 1. Total PAH concentrations measured at discrete sample sites on 16 July and 4 November 1997.

Station	Total PAH (ng·L ⁻¹) July 1997	Total PAH (ng·L ⁻¹) November 1997
SDB01	35	34
SDB02	76	43
SDB03	61	130
SDB04	100	57
SDB05	160	NA
SDB06	190	110
SDB07	120	72
SDB08	200	110
SDB09	38	28
SDB10	39	24
SDB10A	76	46
SDB11	89	62
SDB12	94	100
SDB13	74	59

Sources of PAH in seawater samples can be identified from the relative distribution of the individual PAH analytes measured in each sample (Roberts and Thomas, 1986). Figure 11 shows an example of the relative distribution of PAH in a seawater sample and that of a creosote distribution. Matching patterns of PAH analytes in the samples, particularly the alkylated compounds with known source compounds, provide the source identification. Nearly all the samples from both surveys appear to be derived primarily from a weathered creosote source with a minor component derived from a weathered petroleum product, most likely, diesel fuel. The exception to this general PAH source was seen at the southern end of NAVSTA (SDB08), where the sample appeared to be derived from both weathered fuel and creosote components in roughly equal amounts. This source allocation was seen on both visits, indicating a possible chronic source of the petroleum components.

As mentioned previously, real-time uv-fluorescence has been used successfully as a surrogate measure of TPAH (Katz, et al., 1991). The advantage of using uv-fluorescence is its high sensitivity to PAH, the ability to collect high spatial resolution data in real time, and its low cost. Its disadvantages include a lack of specificity to PAH source types and a requirement to calibrate to a PAH source. The fluorometer used on these surveys was first calibrated to diesel fuel marine (providing units of Diesel Fuel Marine equivalents or DFME), an historical PAH source material in San Diego Bay (Chadwick et al., 1996), to provide a way of normalizing the instrument response

between surveys. The fluorescence data, averaged over the collection period for each discrete sample, were then regressed against the TPAH concentration measured for each sample. Figure 12 shows the result of this calibration.

When all the data are used in the intercalibration, the regression equation accounts for less than 30% of the sample variability ($r^2=0.29$), a result of the low range of observed TPAH values. This result would normally be considered too poor to be used for predictive purposes. When these data are combined with a database developed over the last 8 years, the full regression equation is improved, providing a regression coefficient of 0.61 (figure 13). While far from perfect, this regression equation can reasonably be used to estimate a TPAH value from the uv-fluorescence data when used in the context of a screening tool, or for inter-survey comparisons. Using the uv-fluorescence technique outside the realm of a screening tool would need to be considered on a survey by survey basis.

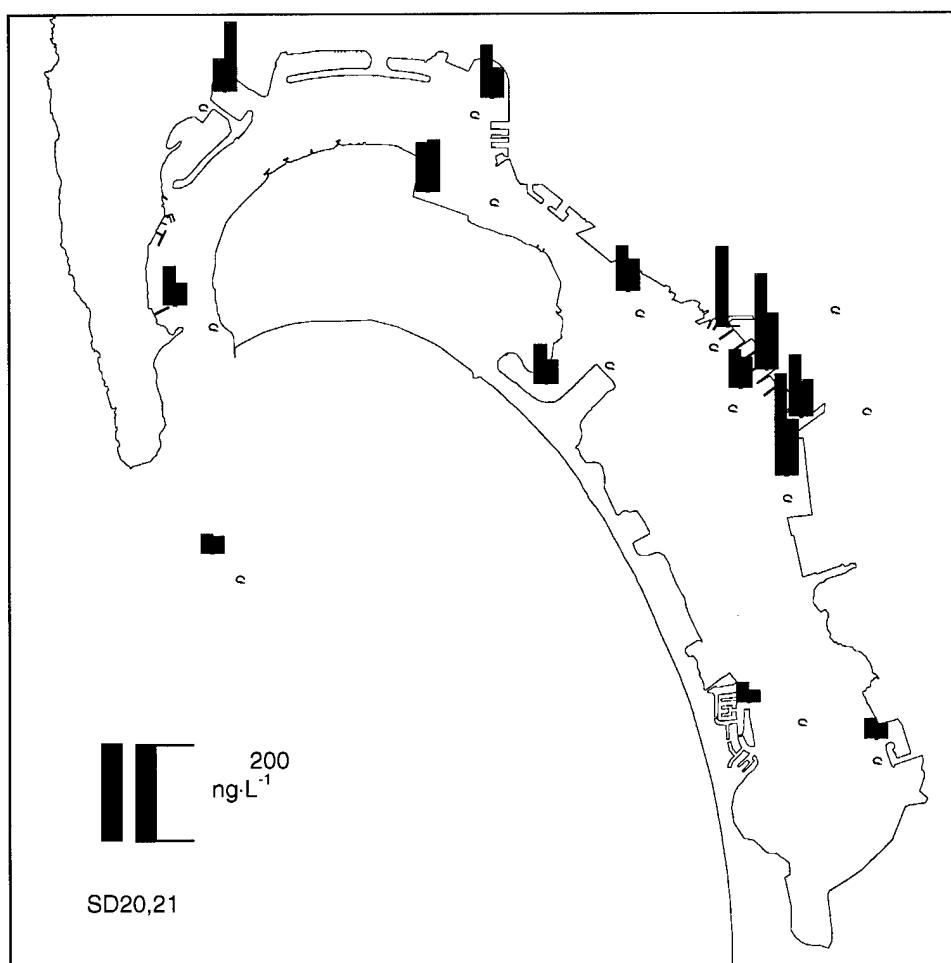


Figure 10. Total PAH concentrations measured at discrete sample sites on 16 July and 4 November 1997. Concentrations are in $\text{ng}\cdot\text{L}^{-1}$.

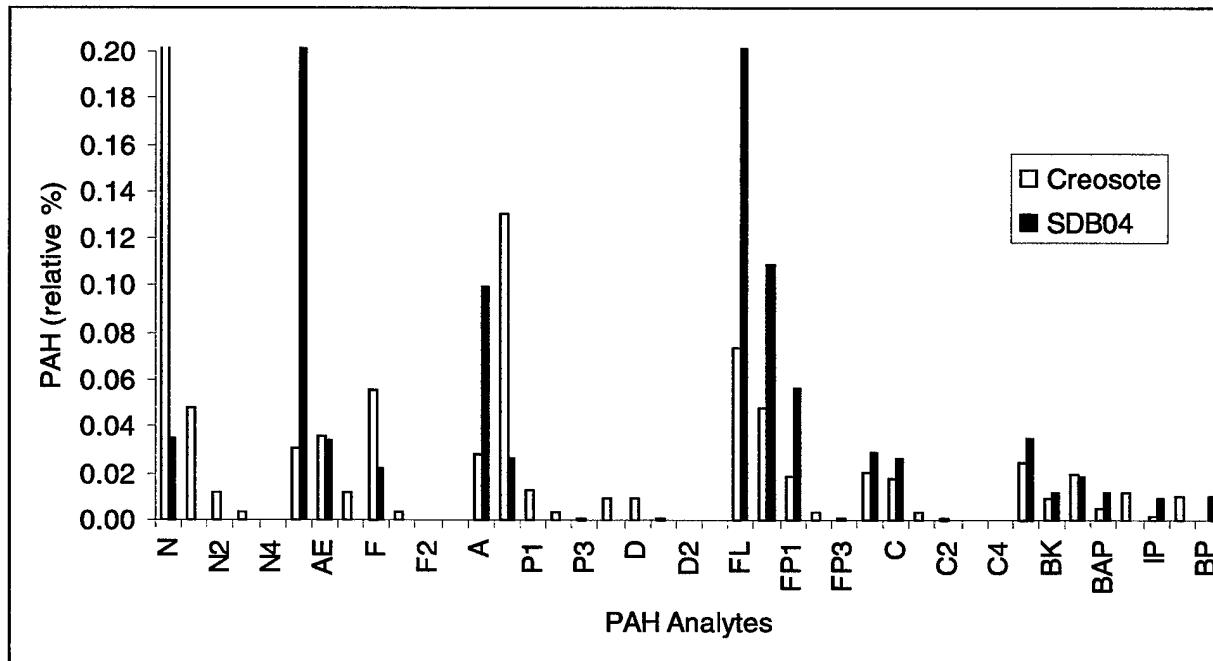


Figure 11. Relative distribution of PAH (%) in sample SDB04 (November) and for a creosote standard. Analyte identifiers are shown in appendix A.

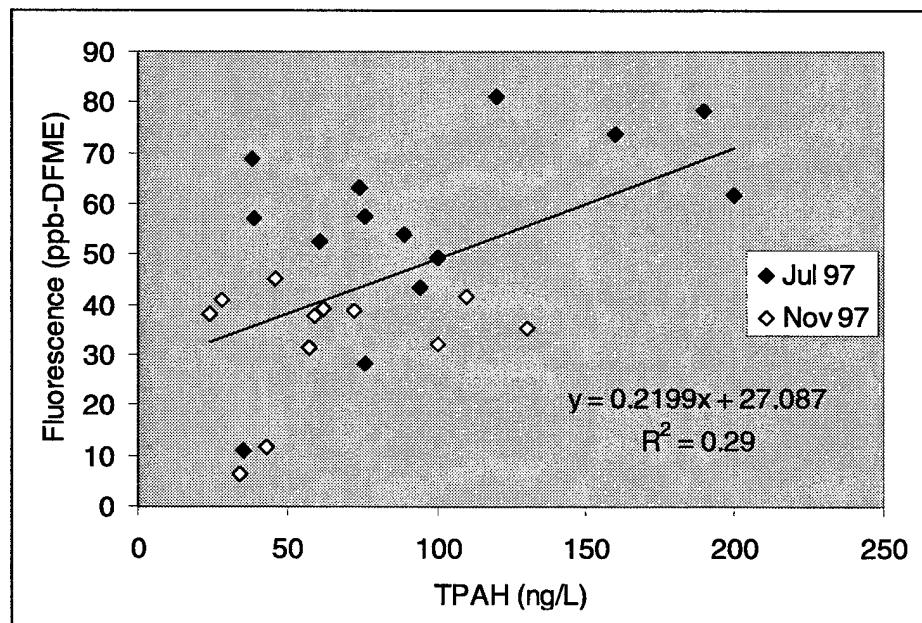


Figure 12. UV-fluorescence (ppb-DFME) regressed against discrete TPAH concentrations ($\text{ng}\cdot\text{L}^{-1}$) for July and November 1997 surveys.

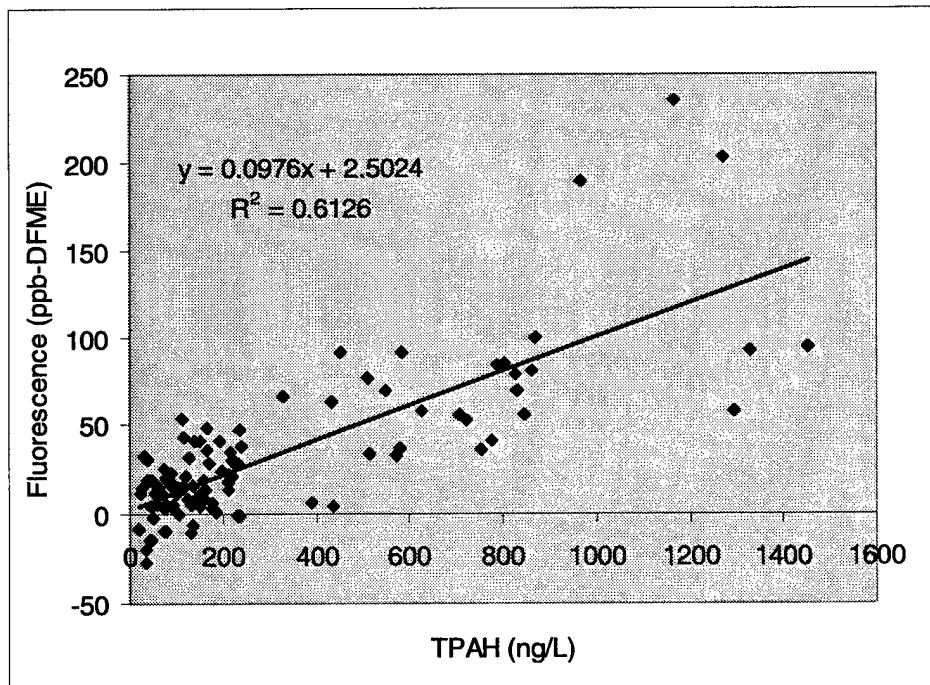


Figure 13. UV-fluorescence (ppb-DFME) regressed against discrete TPAH concentrations ($\text{ng}\cdot\text{L}^{-1}$) for data collected between 1990 and 1997.

The poor intercalibration result on the two recent surveys likely stems from two causes. First, the TPAH data are relatively low, providing too limited a data range for a good regression. Another likely factor is that the DFM calibrant used to normalize the fluorometer between surveys was not a dominant source component in the samples, though historically, it was. For this reason, the uv-fluorescence data should always be calibrated against discrete sample analyses that can provide appropriate detection limits to fingerprinting sources .

Though the original purpose of using the real-time uv-fluorescence data was to increase the spatial resolution of the PAH data, the poor regression relationship on these surveys leads to using the uv-fluorescence only as a qualitative descriptor. Figures 14 and 15 plot relative uv-fluorescence data from the two recent surveys. The main feature of the distribution was a general increase from the mouth into the back bay. The general increase was augmented by relative highs at NAVSTA and in the southernmost region of the back bay on both surveys and in Commercial Basin in November. The relative high in Commercial Basin was coincident with a local dredging operation. As expected, the qualitative distribution of uv-fluorescence followed the general trends observed in the TPAH distribution.

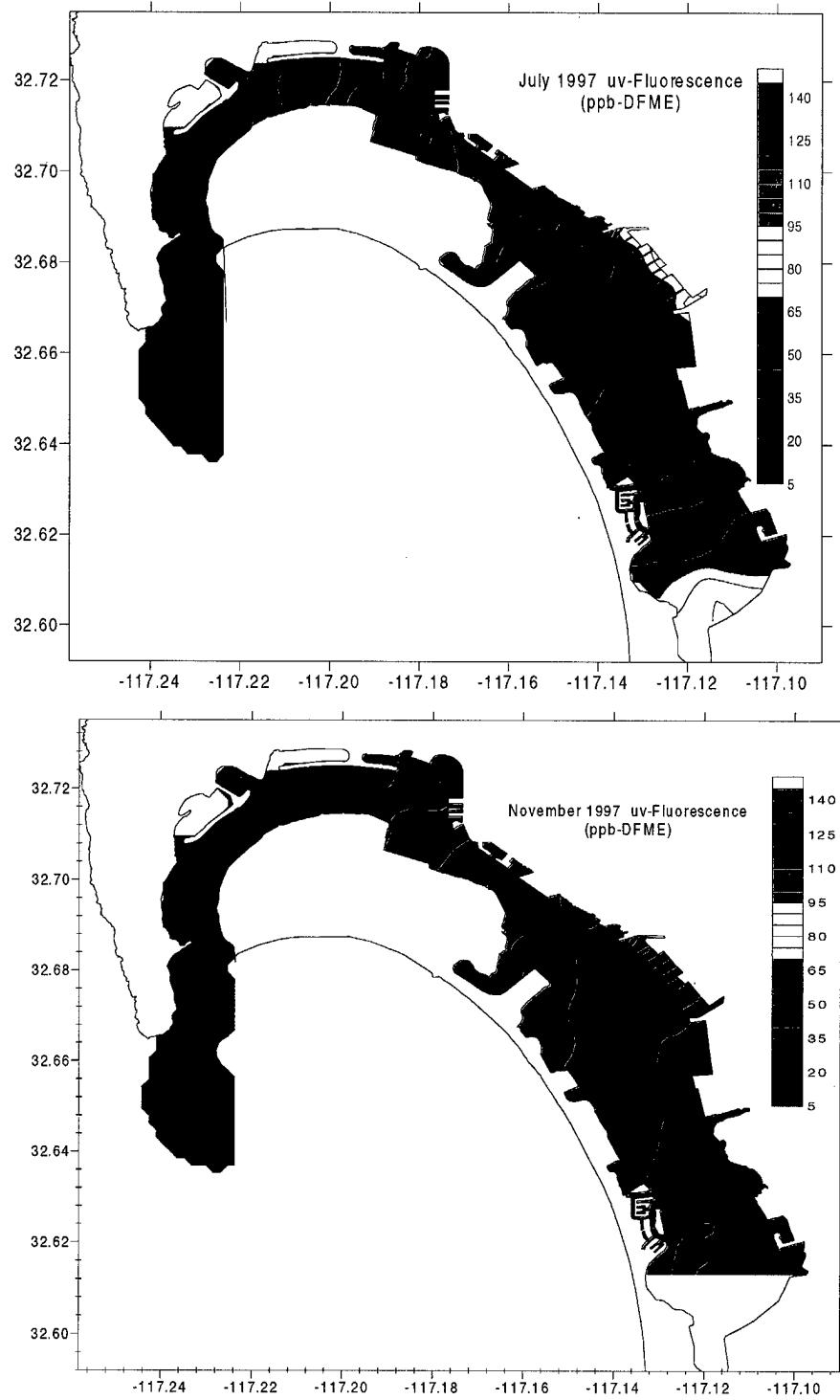


Figure 14. Relative uv-fluorescence distribution (ppb-DFME) for 16 July and 4 November 1997 MESC surveys.

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Table 2 and figure 16 show dissolved Cu concentrations measured on the November survey. Concentrations in the table are derived from the discrete sample data analyzed with EPA-approved methods while those in the figure were derived from the real-time TMA analyses calibrated with the discrete EPA analyses. Concentrations ranged from 0.41 to 4.18 $\mu\text{g}\cdot\text{L}^{-1}$. Maximum concentrations were observed at NAVSTA site SDB08, followed closely at sites within Commercial Basin (SDB03), the entrance to Sweetwater River (SDB18), and in Glorietta Bay (SDB10A). While there was general increase in Cu concentration moving into the bay, the distribution was augmented with inputs from the semi-enclosed basins and at NAVSTA. This distribution was expected because it follows the general pattern and location of ship hulls, a dominant source of Cu.

The data used to develop the spatial distribution in the figure were derived from the real-time TMA analyses calibrated with the EPA approved analyses. The regression, shown in figure 17, was accomplished by comparing the discrete sample splits run on the TMA with those measured using EPA methods. The correlation with a $r^2=0.76$ appears to be quite reasonable for calibration purposes.

Table 2. Dissolved Cu concentrations for discrete stations occupied in November 1997. Concentrations were derived using EPA-approved method 1640.

Station	Dissolved Cu ($\mu\text{g}\cdot\text{L}^{-1}$)	Station	Dissolved Cu ($\mu\text{g}\cdot\text{L}^{-1}$)
SDB01	0.418	SDB10A	3.54
SDB02	0.695	SDB11	2.70
SDB02	0.707	SDB12	2.08
SDB03	3.86	SDB12	2.15
SDB04	2.16	SDB13	3.40
SDB05	3.62	SDB14	0.41
SDB06	3.31	SDB15	1.72
SDB07	3.41	SDB16	3.08
SDB08	4.18	SDB17	3.50
SDB09	2.54	SDB18	3.64

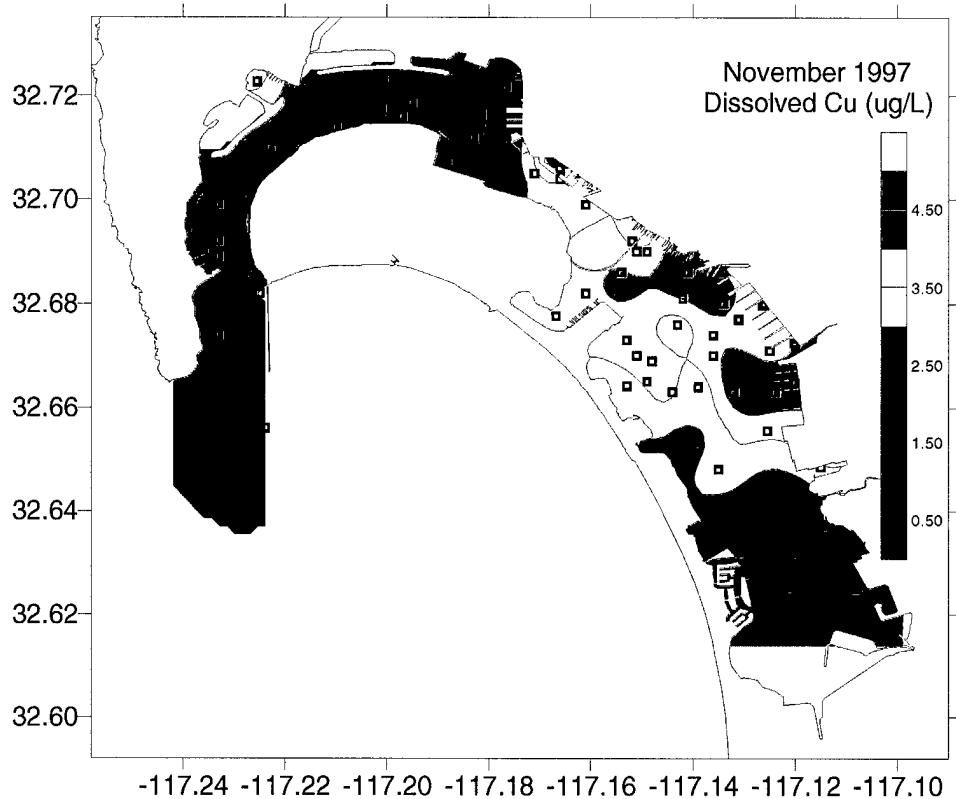


Figure 15. Dissolved Cu($\mu\text{g L}^{-1}$) distribution for 4 November 1997. Concentrations were derived from TMA analyses regressed against EPA analysis. Squares indicate TMA sampling locations.

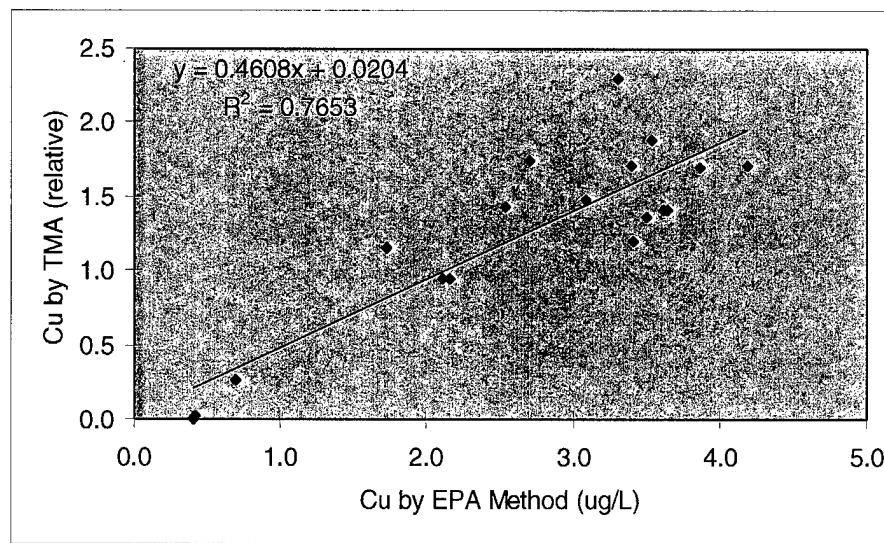


Figure 16. Copper analyzed by TMA regressed against Cu measured by EPA methods. The regression line was used to calibrate all TMA data to extend the spatial resolution of the Cu data collected with discrete samples.

DISCUSSION

REGULATORY PERSPECTIVE

The two 1997 MESC surveys provide snapshots of current San Diego Bay water quality conditions. The surveys can be used for assessing the present environment in the context of regulatory guidelines and long-term trends when compared to historical data sets.

Although not yet adopted by the State of California, the PAH and Cu data will be assessed using the most recent regulatory guideline for water quality criteria, the EPA's proposed California regulatory limits published in August 1997. As mentioned previously, long-term trends will be assessed on a statistical basis.

Though previously regulated as a group, the new guideline for PAH is specific to 16 individual PAH analytes. The criteria, shown in table 3, are based on human health consumption of water and organisms. As such, these are based on chronic concentration levels and, thus, applicable to the measurements made on the surveys. The criteria chronic concentration guideline for Cu is $3.1 \text{ ug}\cdot\text{L}^{-1}$ in dissolved form, while a criteria maximum concentration is $4.8 \text{ ug}\cdot\text{L}^{-1}$. Because the measured concentrations are expected to be the steady-state values, the lower, chronic criterion is the applicable guideline for comparison.

Only two stations measured in July had any analyte concentration that surpassed EPA criteria. In November, all the PAH concentration data were below the EPA criteria. The two sites in July were SDB05 and SDB06 at NAVSTA. At SDB05, benzo(b)fluoranthene and chrysene were reported at $4.6 \text{ ng}\cdot\text{L}^{-1}$. At SDB06, benzo(b)fluoranthene, chrysene, and benzo(a)anthracene were 5.0, 8.0, and $8.4 \text{ ng}\cdot\text{L}^{-1}$, respectively. Note that the measured values were below the analytical reporting limits of $9.6 \text{ ng}\cdot\text{L}^{-1}$, though two samples were concentrated and reanalyzed at a $4.9 \text{ ng}\cdot\text{L}^{-1}$ reporting limit with no significant change in the results. All three PAH components elevated in these samples were likely derived from a creosote source. It is unknown whether creosote-impregnated pier pilings are currently at these sites.

The lack of a measurable concentration above the EPA criteria on the November survey might be related to a real downward concentration trend in the bay. However, the individual analyte concentrations measured on both surveys were exceptionally low and very near the method reporting limits. The implication is that small variations observed from survey to survey might likely be the result of small variations in the analytical quantitation. The impact of these small changes on an analyte basis must, therefore, be carefully considered when imposing regulatory compliance standards.

Nearly half the discrete samples measured for copper surpassed the proposed $3.1 \text{ ug}\cdot\text{L}^{-1}$ water quality criterion, though half of them are less than $0.5 \text{ ug}\cdot\text{L}^{-1}$ higher. The average value for the bay was 2.68. Figure 18 shows the spatial distribution of areas equal to, or exceeding, the regulatory limit using a Hazard Quotient (Measured concentration/Regulated concentration) of greater than 1. Roughly half the bay waters are above the regulatory limit. However, note that measurements were not made at all locations where copper might be elevated. In particular, no measurements were made within semi-enclosed regions of Shelter Island, Harbor Island, Chula Vista Marina, and Coronado Cays, which all contain a high density of boats painted with copper-based paints. However, figure 16 shows the influence of some of these areas on the general distribution of Cu.

Table 3. EPA water quality criteria for PAH as proposed for California, August 1997.

PAH Analyte	EPA Criterion (ng·L ⁻¹)
Acenaphthene	1,200,000
Acenaphthylene	na
Anthracene	9,600,000
Benzo(a)Anthracene	4.4
Benzo(a)Pyrene	4.4
Benzo(b)Fluoranthene	4.4
Benzo(ghi)Perylene	4.4
Benzo(k)Fluoranthene	4.4
Chrysene	4.4
Dibenzo(a,h)Anthracene	4.4
Fluoranthene	300,000
Fluorene	1,300,000
Indeno(1,2,3-cd)Pyrene	4.4
Naphthalene	na
Phenanthrene	na
Pyrene	960,000

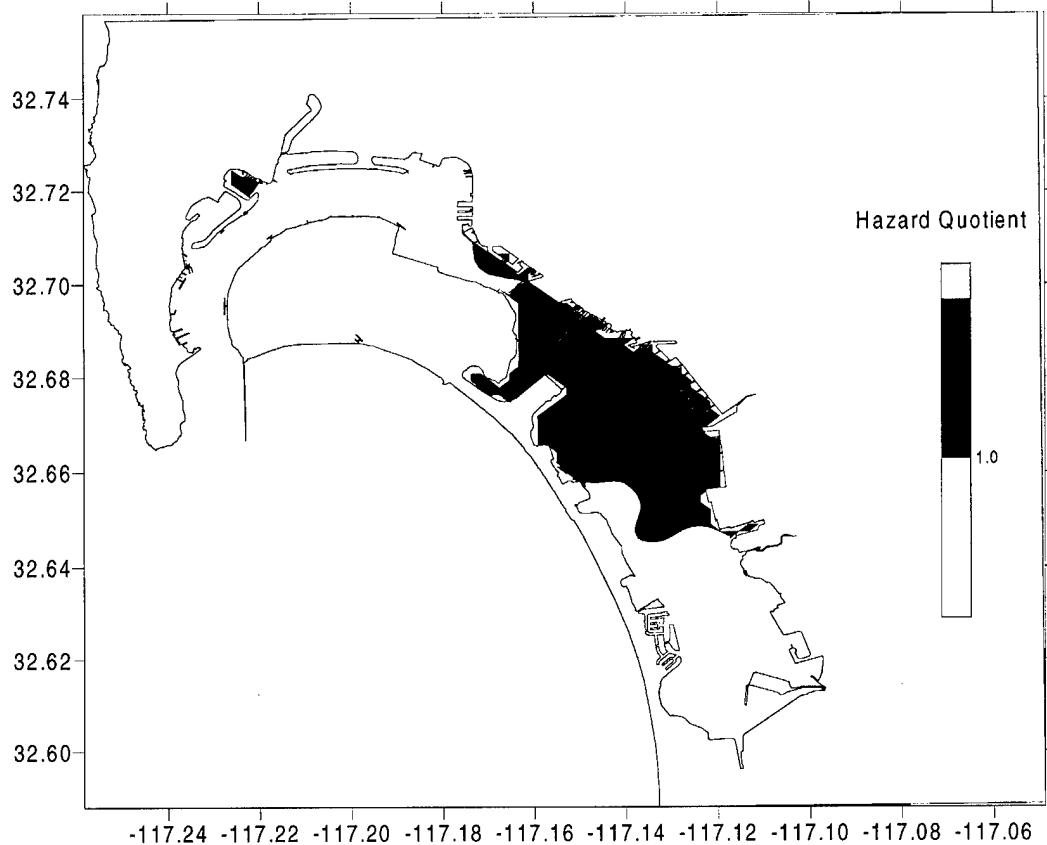


Figure 17. Hazard quotient for Cu using $3.1 \text{ ug}\cdot\text{L}^{-1}$ as regulatory limit. Areas in blue are for values of 1.0 and above.

LONG-TERM TRENDS

The long-term trends of contaminant levels in San Diego Bay will be derived from a statistical analysis of historical data and those collected as part of this study. This analysis can be considered from a bay-wide perspective and to answer the particular question of whether or not operational changes made at NAVSTA have had an impact on concentrations of PAH and Cu in the vicinity of NAVSTA. While statistical methods can be used for this analysis, the outcome still needs to be evaluated within the context of sources and processes affecting the fate and transport of contaminants within the bay, as well as within the regulatory framework.

Polynuclear Aromatic Hydrocarbons

The only known historical seawater PAH concentration data for San Diego Bay come from an unpublished database collected in the last 8 years. The database contains PAH concentration data for 101 samples collected over 10 surveys between March 1990 and May 1994. The samples were collected with MESC at the same locations and analyzed in the same manner as described in the Methods section. While the locations and analyses were the same, the samples were collected during wet and dry season conditions and, occasionally, when a visible oil sheen was clearly present, an indication of recently spilled material.

From a qualitative sense, the historical distribution of uv-fluorescence and TPAH showed the highest concentrations and strongest gradients moving out from the quay walls at NAVSTA. Figure 19 shows an example of this distribution from a MESC survey performed in August 1992. This distribution shows a source of high fluorescence, in this case, well correlated with TPAH, which was unquestionably derived from sources at NAVSTA. Though the magnitude of the fluorescence and TPAH varied over time, this basic distribution was consistently observed on all MESC surveys between 1990 and 1994. Its consistency over temporal scales ranging from tidal variation to seasonal variation indicated chronic sources at NAVSTA. The PAH at NAVSTA were usually derived from a combination of weathered creosote and petroleum products, consistent with an abundance of creosote pilings and fuel products discharged into gravity separators placed in the bay.

Table 4 shows a comparison of historical TPAH data with those collected in the current surveys on a station-by-station basis. The current data, when compared to historical measurements made at the same sites, generally show a marked decrease, particularly in the vicinity of NAVSTA (Sites SDB05, SDB06, SDB07, SDB08, and SDB13). These decreases are significant at the 95% confidence interval at all but three stations: SDB01, SDB03, and SDB06. Having only a single historical concentration value measured at SDB10A in Glorietta Bay precludes a statistical evaluation, though the recent values are over five times lower than the historical value.

At the entrance station, SDB01, the current concentration values are statistically no different than the historical average, even though they are four times lower. This might be expected, given that the site is far from likely sources and has a relatively high mixing rate with clean ocean water. However, the statistical result of "equal means" comes more from the fact that the variability in the historical data was relatively high with a relative standard deviation (rsd) of 117%. This partially results from the fact that on at least one occasion, a sample was collected within a visible sheen from a localized spill. Another reason might be that samples were collected under varying tidal conditions, and given the high flushing at the entrance, samples were collected from "bay" versus "ocean" water. The recent samples were collected from a mostly "ocean" water condition.

While the July sample within Commercial Basin (SDB03) had a TPAH concentration statistically lower than the historical average, the November sample did not. This is likely the result of collecting the November sample during dredge operations. It is expected that once the operation is stopped, that the TPAH levels will return to a similar level seen in July.

Though average TPAH concentrations dropped dramatically at NAVSTA site SDB06, exceptionally high variability in the historical data preclude claiming a statistically significant difference. The high variability seen at this site (rsd= 149%) was caused primarily by a single sample concentration of $>8000 \text{ ng}\cdot\text{L}^{-1}$ collected within a visible sheen. Removal of this sample alone from the statistics would result in a conclusion that the recent measurements of TPAH were statistically reduced from the historical average.

When the TPAH data are pooled at NAVSTA sites SDB05, SDB06, SDB07, SDB08, and SDB13 for both the historical and 1997 data sets, the average value for 1997 is statistically lower than the historical average at the 95% confidence interval (table 5). Pooling the data at all other non-NAVSTA sites gives a similar result in which the 1997 data are statistically lower than the historical average. At NAVSTA sites, the pooled average TPAH dropped by a factor of nine from 1090 to $121 \text{ ng}\cdot\text{L}^{-1}$. At the sites outside NAVSTA, the pooled average TPAH dropped from 158 to $62 \text{ ng}\cdot\text{L}^{-1}$, a drop of more than a factor of two.

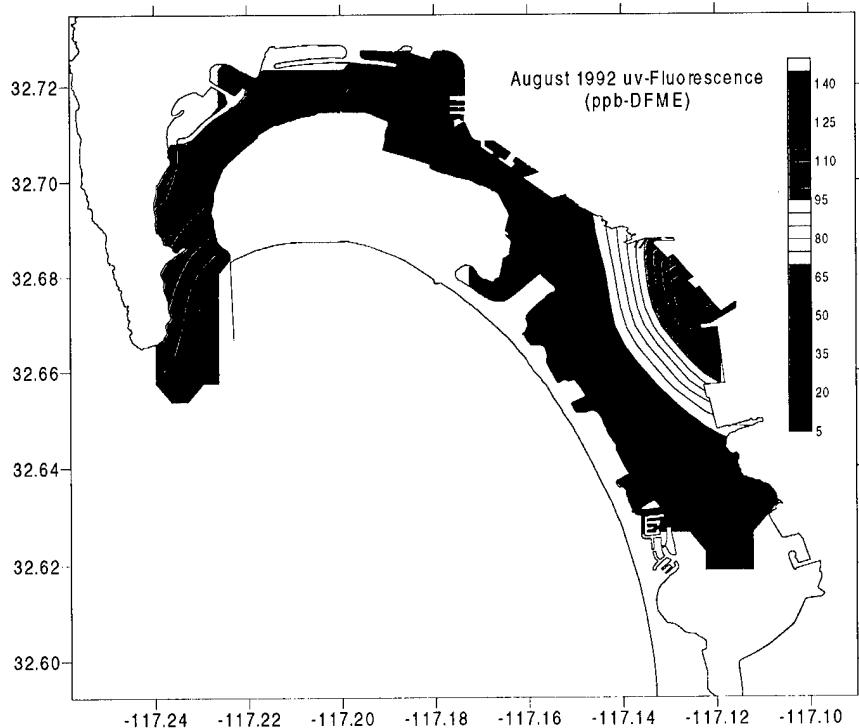


Figure 18. Relative uv-fluorescence distribution (ppb-DFME) for 20 August 1992.

A review of TPAH data pooled for NAVSTA sites shows the high variability observed over time and the significant reduction observed during the last two surveys (figure 20). There is no seasonal or other trend evident in the historical data through 1994. However, a statistical evaluation indicates that the reduction in mean values from July to November 1997 was statistically significant (95%). The implication is that PAH levels in the Bay may still be moving downward, though the impact of stormwater inputs for 1997 are missed in these samplings.

The significant reduction of PAH in the vicinity of NAVSTA can be attributed directly to a reduction of sources at NAVSTA itself. The strong gradients seen historically at NAVSTA (figure 19) were nearly absent on both surveys in 1997 (figures 14 and 15), indicating that not only are the concentrations diminished, but the sources required to support the gradients were also diminished. While the PAH at NAVSTA were historically derived from a combination of weathered creosote and fuel products, the 1997 samples, other than SDB08, showed only a weathered creosote source. Stopping the practice of discharging bilge water into gravity separators located in the bay is directly related to the absence of fuel product PAH seen in the receiving water. This operational change combined with the removal of about half the creosote pier pilings has clearly reduced the overall PAH source dramatically at NAVSTA. The reduction in bay-wide PAH concentrations is also likely a result of the removal of sources at NAVSTA, given the previous strength and persistence of the historical sources.

Table 4. Statistical comparison of historical (1990 to 1994) seawater TPAH data with data collected in 1997 at 13 stations in San Diego Bay. Starred values are not significantly different from the historical mean values at the 95% confidence interval. All concentrations are in units of $\text{ng}\cdot\text{L}^{-1}$.

Station	n	Historical TPAH Average	Historical Standard Deviation	rsd (%)	95% Confidence Interval	Lower Limit 95% Confidence Interval	July 1997	November 1997
SDB01	9	141	166	117	108	33	35*	34*
SDB02	7	239	170	71	126	113	76	43
SDB03	9	155	78	50	51	105	61	130*
SDB04	5	175	37	21	32	143	100	57
SDB05	12	1242	1461	118	826	416	160	-
SDB06	8	1722	2565	149	1777	-55	190*	110*
SDB07	6	697	151	22	121	575	120	72
SDB08	7	723	321	44	238	485	200	110
SDB09	7	98	43	44	32	66	38	28
SDB10	9	83	52	63	34	49	39	24
SDB10A	1	391	-	-	-	-	76*	46*
SDB11	7	177	56	31	41	136	89	62
SDB12	11	181	100	55	59	122	94	100
SDB13	3	434	266	61	301	132	74	59

Table 5. Pooled TPAH data for non-NAVSTA sites and NAVSTA sites. When pooled, the average TPAH values for 1997 are statistically lower than the historical average at the 95% confidence interval. All concentrations are in units of $\text{ng}\cdot\text{L}^{-1}$.

	Non-NAVSTA Sites			NAVSTA Sites		
	n	Average TPAH	Standard Deviation	n	Average TPAH	Standard Deviation
Historical	65	158.1	110.9	36	1089.6	1483.6
1997	18	61.6	28.4	9	121.3	52.0

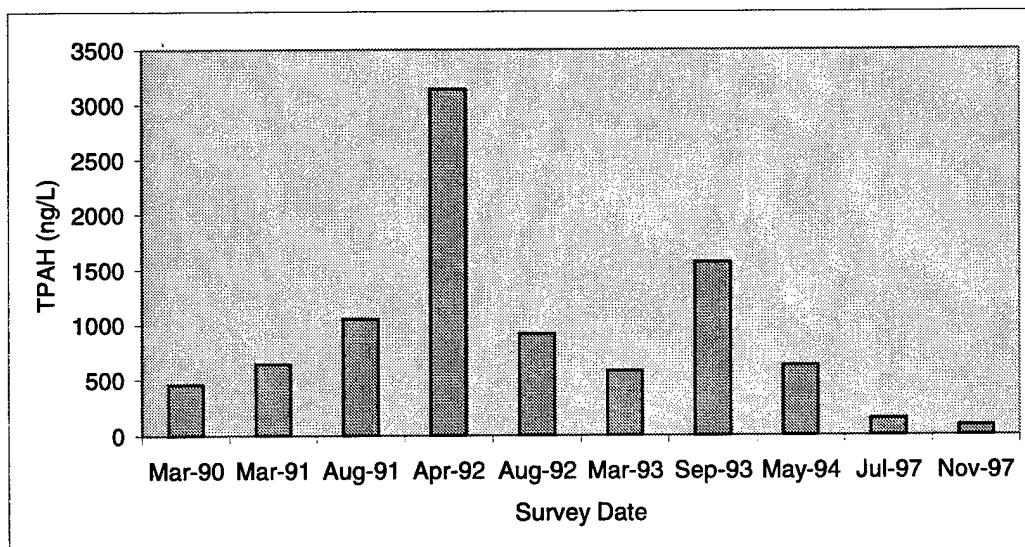


Figure 19. Average TPAH values for NAVSTA sites measured from 1990 to 1997.

Copper

Historical seawater Cu data from 1989 to 1993 show dissolved concentrations in the range of 0.3 to about 7 $\mu\text{g}\cdot\text{L}^{-1}$ (Valkirs et al., 1994; Flegal and Sanudo-Wilhelmy, 1993). The average bay-wide concentration of Cu for these data sets was 3.2 $\mu\text{g}\cdot\text{L}^{-1}$. The historical distribution of Cu generally shows an increase from the open ocean into the back bay. Occasional high values were observed in the semi-enclosed regions of Shelter Island and Glorietta Bay. As such, the current distribution and concentrations of Cu measured in 1997 are not unlike that measured in the past. This is borne out in a comparison of a June 1992 data set (Valkirs et al., 1994) with the 1997 data, even though the site locations were not exactly the same (figure 21).

While the average 1997 Cu concentration pooled for NAVSTA sites is not statistically different than the historical average, the pooled 1997 average at non-NAVSTA sites is statistically lower than the historical average (table 6). The lack of change in Cu concentrations within the NAVSTA region is reasonable in light of the fact that there have not been any significant changes in the use of copper anti-fouling coatings or in operations there with respect to Cu. The reason for the reduction at non-NAVSTA sites is not known, but may possibly be tied to improved trace metal analytical methods. Monitoring bay-wide concentrations further would allow future trends to be better understood.

Table 6. Pooled dissolved Cu data for non-NAVSTA sites and NAVSTA. For NAVSTA sites, the pooled averages are not statistically different. All concentrations are in units of $\mu\text{g}\cdot\text{L}^{-1}$.

	Non-NAVSTA Sites			NAVSTA Sites		
	n	Average Cu	Standard Deviation	n	Average Cu	Standard Deviation
Historical	45	3.08	1.54	17	3.52	0.949
1997	14	2.22	1.26	5	3.59	0.35

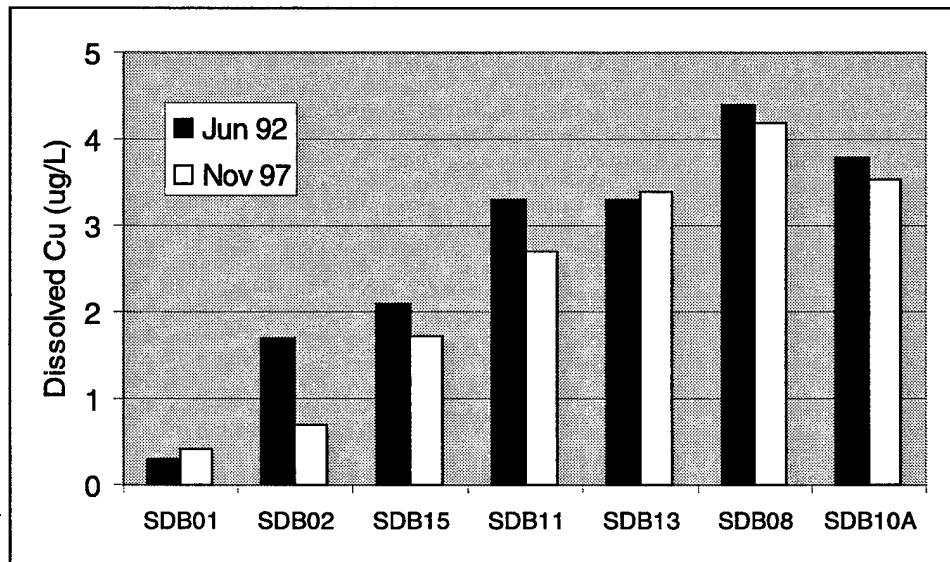


Figure 20. Dissolved Cu concentrations ($\mu\text{g}\cdot\text{L}^{-1}$) measured in June 1992 and in November 1997 at similar sites.

CONCLUSIONS

This study provided a unique opportunity to assess long-term trends in water quality, particularly with regards to PAH and Cu concentrations in San Diego Bay. With recent changes occurring in operational practices at NAVSTA, this opportunity extends to a direct assessment of how those changes have, or have not, impacted levels of dissolved PAH and Cu in the bay. Combining the recent measurements with a rich historical database allowed the trends to be quantified statistically with a high degree of confidence.

The study used MSEC's unique capabilities to provide the appropriate multiparameter, synoptic data to characterize distributions at sufficient spatial resolution to identify sources. It also used analytical capabilities that provided detection limits low enough for comparison to EPA criteria as well as for fingerprinting PAH sources.

POLYNUCLEAR AROMATIC HYDROCARBONS

The general distribution of seawater PAH is consistent with known sources and flushing characteristics of the bay. Concentrations increase into the bay as a result of increased sources, primarily creosote pilings and lower flushing. The PAH were derived primarily from weathered creosote sources, except for NAVSTA site SDB08 at the entrance to Paletta Creek, which showed an additional and, potentially chronic, weathered fuel product source.

In general, PAH concentrations measured in 1997 were the lowest measured in the bay during the last 7 years. This is borne out by comparison of recent and historical distributions of uv-fluorescence showing reduced gradients as well as from a statistical evaluation of the PAH. On a site-by-site basis, all sites showed lower concentrations than the historical average. However, at two sites, one at the entrance and one at NAVSTA, the lower values were not statistically significant, primarily a result of high variability in the historical database. On a regional basis, PAH at NAVSTA sites were

significantly lower than the historical average as were sites outside the NAVSTA region. The reduction in concentrations at NAVSTA can be directly attributed to the reduction of sources at NAVSTA itself. The reduction outside the NAVSTA region also likely results partially from the removal of sources at NAVSTA, given the previous strength and persistence of the historical sources.

From a regulatory standpoint, the PAH measured in November were all below proposed EPA criteria. The July sampling, however, showed two sites at NAVSTA having three analytes (of 16 regulated) surpassing water quality criteria. The measured concentrations were at, or near the method-reporting limit, and should be critically reviewed when imposing compliance standards. It is not known whether the reduction of analyte concentrations from above to below the criteria between July and November is, therefore, the result of a real trend or analytical variation.

COPPER

The general distribution of dissolved Cu in San Diego Bay is consistent with known sources. The general increase in concentrations into the back bay, and localized increases associated with marinas and NAVSTA, follows the distribution of ship hulls containing copper-based paints and flushing characteristics of the bay. The result is that copper concentrations surpass the proposed regulatory criterion in roughly half the bay. The fact that recent concentrations measured in the vicinity of NAVSTA are not statistically different than those measured historically is consistent with the fact that there has not been a significant change in operations affecting sources there. Conversely, the statistically significant decrease seen in recent Cu concentrations for sites outside the NAVSTA region may imply that sources may have been reduced, though this would need to be verified with continued monitoring.

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APPENDIX A
Polynuclear Aromatic Hydrocarbons Analysis Report

**Arthur D Little, Inc.
Cambridge, MA 02140**

January 9, 1998

Charles N. Katz
Principal Investigator
NCCOSC RDTE DIV D362
53475 Strothe Road. Rm. 258
San Diego, CA 92152-5410

Re: Data Interpretation for Second Round of Water Samples, Delivery Order 7

Dear Chuck:

As agreed, I have evaluated the PAH results of the second round of seawater samples using the same criteria as before to allocate PAH distributions to creosote and diesel sources. In addition I have compared the total PAH with shifts in the distribution patterns to further characterize the PAH fingerprints.

Summary

Seawater samples were analyzed from 14 sites at two different time periods. PAH distributions found in all samples correspond to weathered creosote. One sample, SDB08, also contains PAH distributions corresponding to weathered diesel. Total PAH concentration diminished from sampling round one to round two by 0 to 45 percent. The analysis of sample SDB12 result in additional PAH distributions not present in the analysis from round 1, however, these distributions can be attributed to weathered creosote PAHs possibly found in suspended solids in the water.

PAH Allocations to Creosote and Diesel

The compounds have been allocated to the most likely source by inspection of the PAH distribution patterns. **Figures 1 and 2** are graphs of the PAH distribution for diesel and creosote respectively. In the creosote profile, **Figure 1**, the concentrations of parent to alkylated PAH decrease exponentially. In a fresh diesel profile, **Figure 2**, there is an increase in concentration from parent through C3-alkylated compounds then a decrease to the C4-alkylated compounds. Since many of the PAH compounds are found in both sources a true allocation of PAH distributions is not possible. However, selecting for the unique constituents of the patterns can perform a conservative estimate and allocating the rest based on importance to the source oil patterns.

PAH compounds allocated to creosote, which are unique to creosote or substantially important components in the creosote patterns, are: naphthalene, acenaphthalene, fluorene, anthracene, phenanthrene, fluoranthene, pyrene, fluoranthene/pyrenes, chrysenes, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, perylene, indeno[1,2,3,-c,d]pyrene, dibenzo[a,h]anthracene, benzo[g,h,i]perylene. Diesel

is allocated the rest, which include: C1- through C4- naphthalenes, acenaphthene, biphenyl, C1- through C3-fluorenes, C1- through C4-phenanthrenes, and the dibenzothiophenes. The dibenzothiophenes, critical indicators of petroleum products, are resistant to weathering and the C2- and C3- alkylated homologues are found only at low levels in creosote. Acenaphthalene is a unique tracer for creosote. **Table 1** is a complete list of PAHs assigned to the creosote and diesel allocations.

PAH Distributions in Weathered Sources

The seawater samples from this study typically contain weathered PAH distribution profiles. Weathering comes from a variety of influences: dissolution, evaporation, adherence, chemical and photochemical reactions, and biodegradation. In weathered samples the relative concentration of PAH compounds shifts to an exponential increase from parent through C4-alkylated compounds. Although weathered creosote profiles still maintain the emphasis on parent PAH homologue concentrations, there is a shift in relative concentrations from naphthalenes in fresh creosote to fluoranthenes/pyrenes in weathered creosote.

Seawater Sample PAH Distributions

As before the seawater samples have all been allocated to a creosote source with one sample, SDB08-SD21 partially allocated to a weathered diesel source. In general the patterns are more weathered than before containing mostly parent PAH compounds. There is also an increase in the relative distribution of acenaphthalene, characteristic to creosote, as well as a decrease in the relative distribution of the later eluting PAHs benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, perylene, indeno[1,2,3,-c,d]pyrene, dibenzo[a,h]anthracene, benzo[g,h,i]perylene. **Figure 3** contains a weathered creosote PAH distribution for sample SDB04-SD21.

Sample SDB08-SD21 has a more interesting mix of both creosote and petroleum alkylated PAH profiles, as illustrated in **Figure 4**. The naphthalenes, fluorenes, fluoranthene/pyrenes and later PAH compounds, benzo[b]fluoranthene through benzo[g,h,i]pyrene follow the weathered creosote pattern. However, the presence of phenanthrene/anthracenes and dibenzothiophenes with concentration profiles increasing from parent to C4-alkylated PAHs is characteristic of weathered petroleum. This sample has been allocated an estimated mix of 30% petroleum, possibly diesel, and 70% creosote sources, **Table 2**.

Sample SDB12-SD21 contains the creosote patterns described above with some additional PAH homologue compounds, C1- to C4-fluoranthene/pyrenes and C1-chrysenes, which are part of a weathered creosote fingerprint. These PAH homologues are uncharacteristic of water-soluble PAH compounds, but could have come from suspended solids disturbed from the bottom or other source in the area.

Table 3 summarizes total PAH for both sampling rounds. Samples range from near 0 to 45 percent reduced in total PAH. This is demonstrated graphically in a histogram, **Figure 5**. One sample, SDB12-SD21, has an increase in total PAH which is due to the additional PAH homologues present as described above. Sample SDB03-SD21 was lost during shipment and has no data.

If you have any questions please do not hesitate to call me at 617-498-5163 or Gregg at 617-498-5384.

Sincerely,

Neal Yarranton
Deputy Project Manager, NRaD Projects.

Table 1 Petroleum and Creosote PAH Allocation Lists

Petroleum (Diesel) Allocation	Creosote Allocation
C1-Naphthalenes	Naphthalene
C2-Naphthalenes	Acenaphthylene
C3-Naphthalenes	Fluorene
C4-Naphthalenes	Anthracene
Acenaphthene	Phenanthrene
Biphenyl	Fluoranthene
C1-Fluorenes	Pyrene
C2-Fluorenes	C1-Fluoranthenes/pyrenes
C3-Fluorenes	C2-Fluoranthenes/pyrenes
C1-Phenanthrenes/anthracenes	C3-Fluoranthenes/pyrenes
C2-Phenanthrenes/anthracenes	Benzo[a]anthracene
C3-Phenanthrenes/anthracenes	Chrysene
C4-Phenanthrenes/anthracenes	C1-Chrysene
Dibenzothiophene	C2-Chrysene
C1-Dibenzothiophenes	C3-Chrysene
C2-Dibenzothiophenes	C4-Chrysene
C3-Dibenzothiophenes	Benzo[b]fluoranthene
	Benzo[k]fluoranthene
	Benzo[e]pyrene
	Benzo[a]pyrene
	Perylene
	Indeno[1,2,3,-c,d]pyrene
	Dibenzo[a,h]anthracene
	Benzo[g,h,i]perylene

January 9, 1998

Charles N. Katz
Principal Investigator
NCCOSC RDTE DIV D362

Table 2 Estimated Petroleum and Creosote Allocation of Samples

Field ID	First Sample Round			Second Sample Round		
	Allocation	% Creosote	% Diesel	Field ID	Allocation	% Creosote
Creosote	Creosote	85	15	Creosote	Creosote	85
Diesel	Diesel	9	91	Diesel	Diesel	9
SDB1-20	Creosote/Diesel	80	20	SDB01-SD21	Creosote	100
SDB2-20	Creosote	86	14	SDB02-SD21	Creosote	100
SDB3-20	Creosote	90	10	SDB03-SD21	Creosote	N/A
SDB4-20	Creosote	87	13	SDB04-SD21	Creosote	100
SDB5-20	Creosote/Diesel	83	17	SDB05-SD21	Creosote	100
SDB6-20	Creosote	85	15	SDB06-SD21	Creosote	96
SDB7-20	Creosote/Diesel	82	17	SDB07-SD21	Creosote	94
SDB8-20	Creosote/Diesel	58	42	SDB08-SD21	Creosote/Diesel	70
SDB9-20	Creosote/Diesel	81	19	SDB09-SD21	Creosote	100
SDB10-20	Creosote/Diesel	82	18	SDB10-SD21	Creosote	100
SDB10A-20	Creosote	90	10	SDB10A-SD21	Creosote	100
SDB11-20	Creosote	86	14	SDB11-SD21	Creosote	100
SDB12-20	Creosote	85	15	SDB12-SD21	Creosote	100
SDB13-20	Creosote	87	13	SDB13-SD21	Creosote	100

January 9, 1998

Charles N. Katz
Principal Investigator
NCCOSC RDTE DIV D362

January 9, 1998

Charles N. Katz
Principal Investigator
NCCOSC RDTE DIV D362

Field ID	Total PAH SD20	Total PAH SD21	% Reduced
SDB01	35	34	2.8
SDB02	76	43	43
SDB03	61	N/A	N/A
SDB04	100	57	43
SDB05	160	130	19
SDB06	190	110	42
SDB07	120	72	40
SDB08	200	110	45
SDB09	38	28	26
SDB10	39	24	38
SDB10A	76	46	39
SDB11	89	62	30
SDB12	94	100	-6.4
SDB13	74	59	20

Figure 1 Characteristic Creosote Profile

Analyte Profile Histogram

"96B3803 DIL: Creosote Oil"

The Creosote profile decreases exponentially from parent to C4-alkylated homologues.

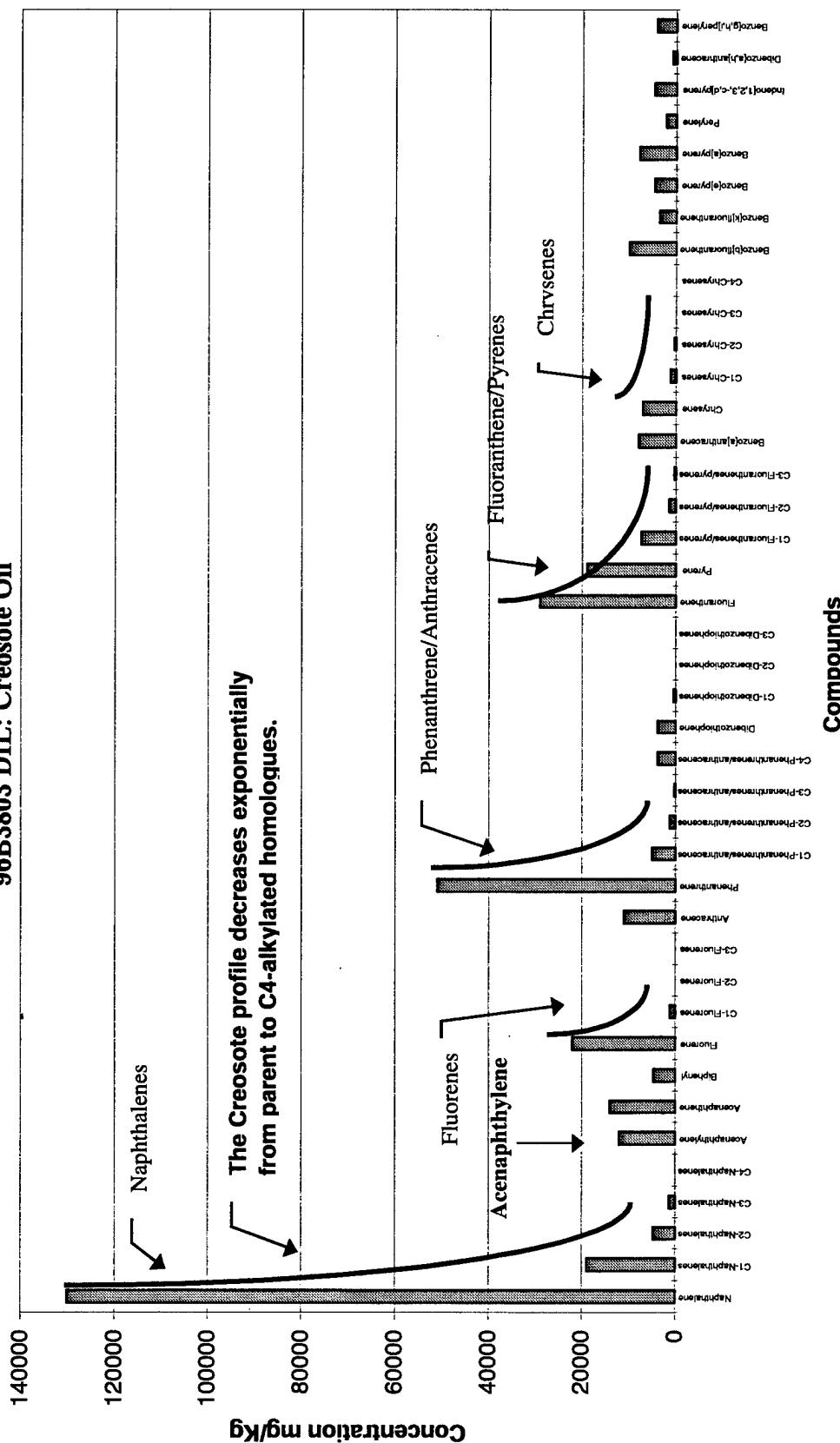


Figure 2 Characteristic Diesel Profile Analyte Profile Histogram

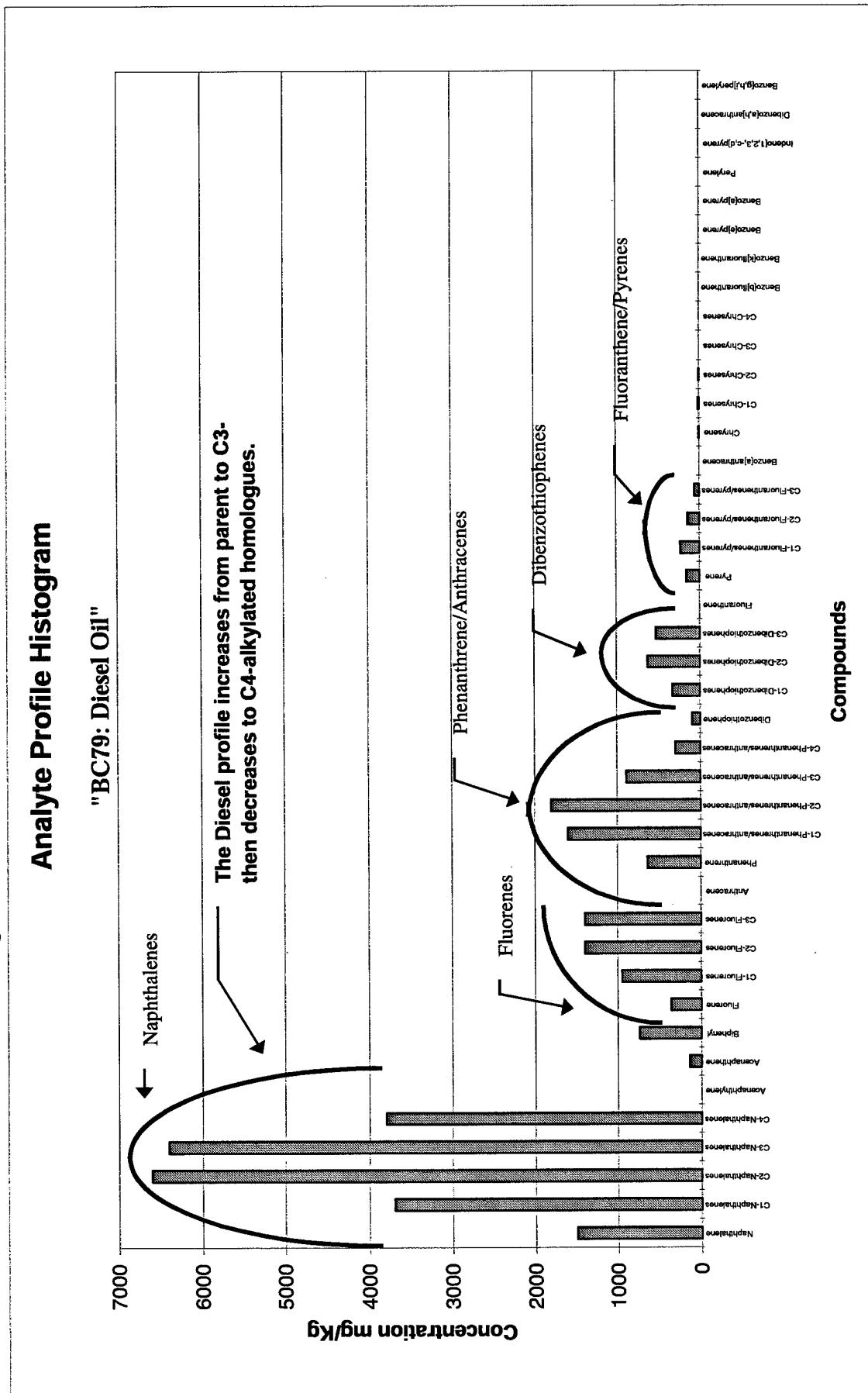


Figure 3 Weathered Creosote Profiles in a Seawater Sample

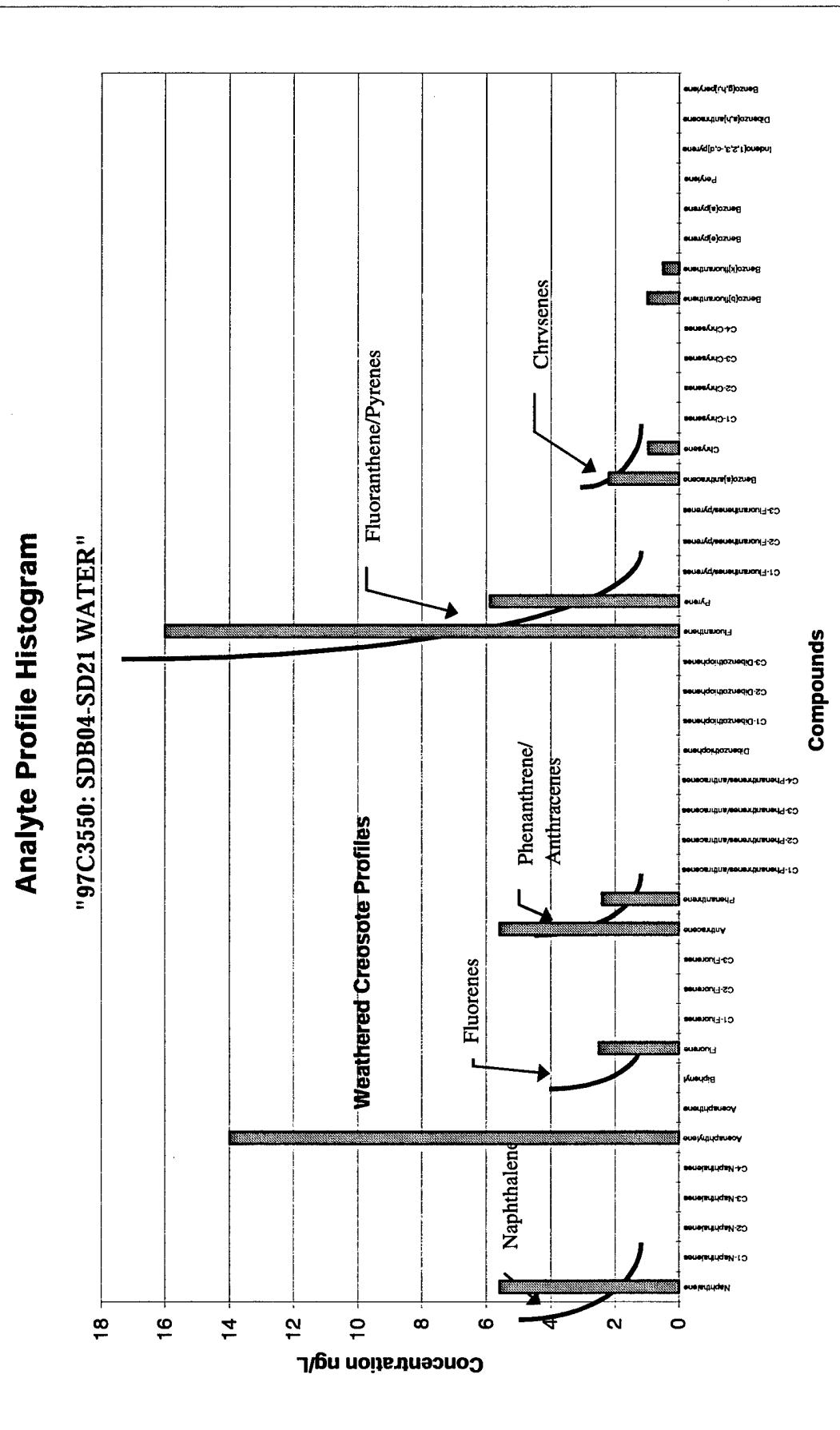


Figure 4 Combined Weathered Creosote/Petroleum Profiles in a Seawater Sample

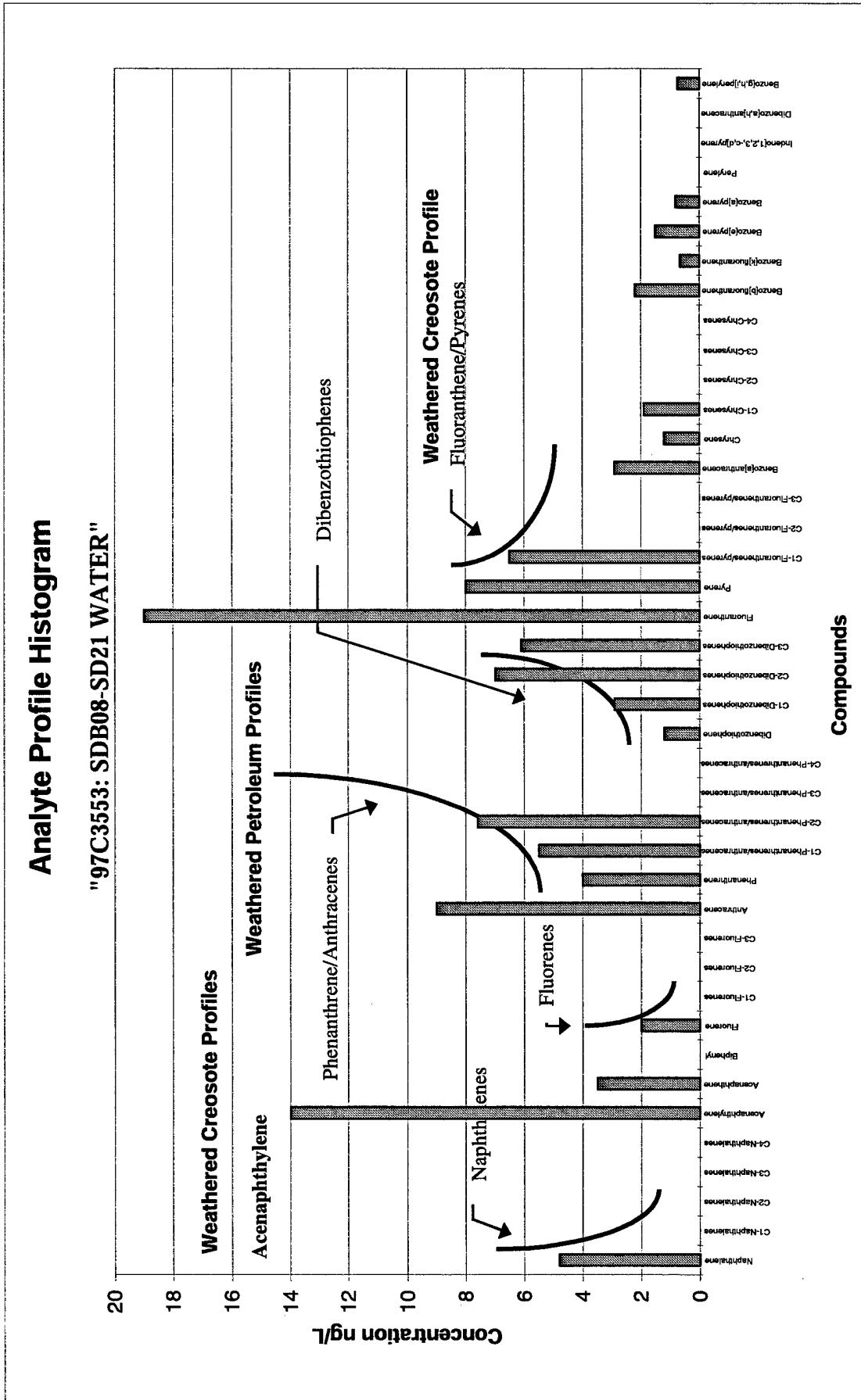
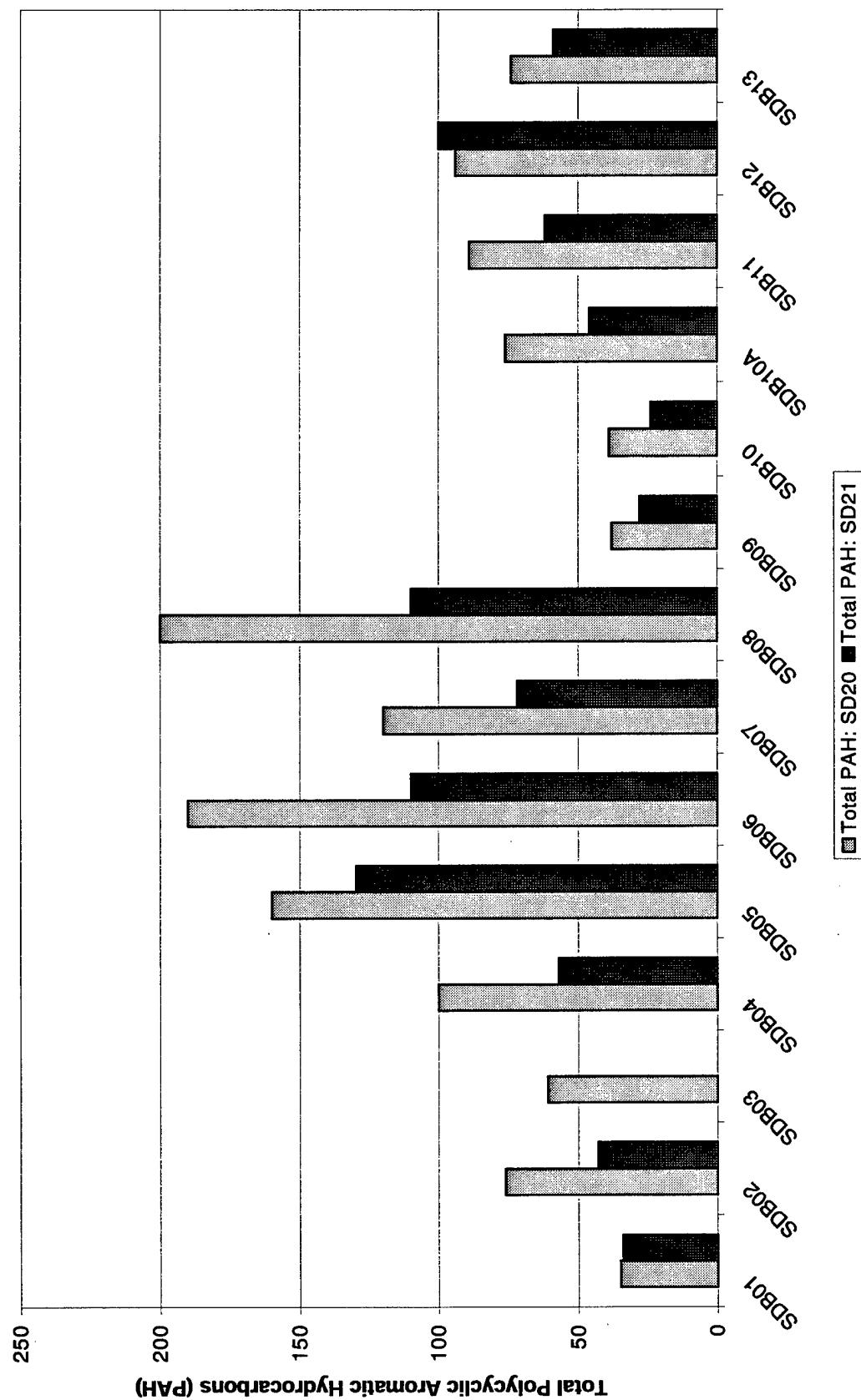


Figure 5 Total PAH in Seawater from Sampling Events SD20 and SD21



**APPENDIX B
COPPER ANALYSIS REPORT**

**Battelle Marine Sciences Laboratory
Sequim, WA 98382**

January 6, 1998

Mr. Chuck Katz
NCCOSC RDTE Div 522
53475 Strothe Road
San Diego, CA 92152

Dear Chuck:

Enclosed are the results for dissolved Cu in San Diego Bay seawater and metals in water samples (mainly dissolved) from Sinclair Inlet. The metals in the seawater samples were preconcentrated by tetrahydroborate reductive precipitation (Nakashima et al., 1988) then quantified by ICP-MS (EPA Method 1640). The Ag in the Sinclair effluent samples was determined by direct analysis using ICP-MS (Method 1638). To improve the detection limit for Ag in the Sinclair seawater samples, we preconcentrated the Ag using the preconcentration method of Bloom and Crecelius (1984) with quantification by ICP-MS.

The Cu concentrations in San Diego Bay ranged from 0.4 to 6.1 $\mu\text{g/L}$. The high Cu concentrations in samples SD1 and SD2 are the results of the higher acid concentration in these two samples. I did a storage test with 2% HNO_3 in these two bottles and measured 0.5 $\mu\text{g/L}$ Cu, which indicates the bottles are not very clean. The two procedural blanks contained 0.03 and 0.06 $\mu\text{g/L}$ Cu. The detection limit is 0.1 $\mu\text{g/L}$. The results for the SRM CASS-3 are higher than the certified range of Cu (0.46 to 0.58 $\mu\text{g/L}$). Matrix spike recoveries were good.

The results for Sinclair Inlet samples are typical for Puget Sound urban bays. The results are blank corrected for the procedural blank, which contained detectable Cr, Cu, and Zn. The results for SRMs and matrix spikes were generally good. The results for Cr and Pd were about 0.01 $\mu\text{g/L}$ high for CASS-3.

If you have questions please call me at 360/681-3604.

Sincerely,

Eric Crecelius
Technical Group Manager
Marine Chemistry and Ocean Processes

:at

Enclosures: Table – Sinclair Inlet
Table – SSC San Diego

BATTELLE MARINE SCIENCES LABORATORY

1529 West Sequim Bay Road

Sequim, WA 98382-9099

360/681-

3604

SSC SAN DIEGO

Cu in Water
Samples Received 11/6/97

MSL Code	Sponsor ID	Cu (μ g/L)
1143-58	SDB10-SD21	6.10
1143-59	SDB19-SD21	5.38
1143-60	SDB07-SD21	3.41
1143-61	SDB17-SD21	3.50
1143-62	SDB15-SD21	1.72
1143-63	SDB16-SD21	3.08
1143-64	SDB18-SD21	3.64
1143-65	SDB06-SD21	3.31
1143-66 r1	SDB02-SD21	0.695
1143-66 r2	SDB02-SD21	0.707
1143-67	SDB04-SD21	2.16
1143-68	SDB09-SD21	2.54
1143-69	SDB03-SD21	3.86
1143-70	SDB08-SD21	4.18
1143-71	SDB05-SD21	3.62
1143-72 r1	SDB12-SD21	2.08
1143-72 r2	SDB12-SD21	2.15
1143-73	SDB11-SD21	2.70
1143-74	SDB01-SD21	0.418
1143-75	SDB14-SD21	0.410
1143-76	SDB13-SD21	3.40
1143-77	SDB10A-SD21	3.54

BLANKS

1143-blk r1	0.0634
1143-blk r2	0.0280

REPLICATE ANALYSIS

1143-66 r1	SDB02-SD21	0.695
1143-66 r2	SDB02-SD21	0.707
RPD		2%

Approvals:

Project Manager

Date

QA/QC Officer

Date

REPLICATE ANALYSIS

1143-72 r1	SDB12-SD21	2.08
1143-72 r2	SDB12-SD21	2.15
	RPD	3%

STANDARD REFERENCE MATERIAL

1643d Direct	20.4
1643d Direct	21.3
1643d Direct	21.1

certified value	20.5
range	± 3.8
percent difference	0%
	4%
	3%

cass3 r1	0.661
cass3 r2	0.669

certified value	0.517
range	± 0.062
percent difference	28%
	29%

MATRIX SPIKE RESULTS

Amount Spiked	5.00
1143-66 mean	0.701
1143-66 MS	5.64
Amount Recovered	4.94
Percent Recovery	99%

Amount Spiked	5.00
1143-72 mean	2.11
1143-72 MS	7.12
Amount Recovered	5.01
Percent Recovery	100%

RPD Relative percent difference

Mr. Chuck Katz
January 6, 1998

References:

Bloom, N. S., and E. A. Crecelius. 1984. "Determination of Silver in Sea Water by Coprecipitation with Cobalt Pyrrolidinedithiocarbamate and Zeeman Graphite-Furnace Atomic Absorption Spectrometry. *Anal. Chim. Acta.* 156:139-145.

Nakashima, S., R. E. Sturgeon, N. S. Willie, and S. S. Berman. 1988. Determination of trace elements in seawater by graphite-furnace atomic absorption spectrometry after preconcentration by tetrahydroborate reductive precipitation. *Anal. Chim. Acta* 207:291-299.

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6. AUTHOR(S)		8. PERFORMING ORGANIZATION REPORT NUMBER	
C. N. Katz		TR 1768	
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12a. DISTRIBUTION/AVAILABILITY STATEMENT		13. ABSTRACT (Maximum 200 words)	
Approved for public release; distribution is unlimited.		Water quality measurements were made throughout San Diego Bay in 1997 as part of the Navy's efforts to assess current environmental conditions in the bay. The water quality measurements focused on polynuclear aromatic hydrocarbons and copper concentrations, compounds that have been identified as chemical contaminants of concern by the San Diego Bay Interagency Water Quality Control Panel. The effort was designed to assess how recent changes in bilge water operations and the removal of creosote-impregnated pier pilings at Naval Station, San Diego, may have impacted the steady-state concentrations of these contaminants in the waters of San Diego Bay.	
Concentrations of PAH were the lowest measured in the bay in the last 8 years. Recent PAH levels at NAVSTA sites compared with those measured historically are significantly lower by a factor of nine. Non-NAVSTA sites were also significantly lower by more than a factor of two. Based on the historical distribution of sources and source types, the reduction in PAH concentrations at NAVSTA sites and, perhaps, the rest of the bay, can be attributed directly to the change in operations at NAVSTA. While recent Cu concentrations were not statistically different from those measured historically at NAVSTA sites, the remainder of the bay had significantly lower concentrations. Operational changes at NAVSTA have not impacted Cu concentrations in the bay.		14. SUBJECT TERMS	
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		UNCLASSIFIED	
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		SAME AS REPORT	

21a. NAME OF RESPONSIBLE INDIVIDUAL C. N. Katz	21b. TELEPHONE <i>(include Area Code)</i> (619) 553-5332 e-mail: ckatz@spawar.navy.mil	21c. OFFICE SYMBOL Code D362

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